FeSe – a simple superconductor?

Claudia Felser

Vadim Ksenofontov, Fred Casper, Shahab Naghavi

T. M. McQueen, A. J. Williams, R. J. Cava

S. Medvedev, I. Trojan, T. Palasyuk, Mikhail I. Eremets,

G. Wortmann

Universität Mainz

University of Princeton

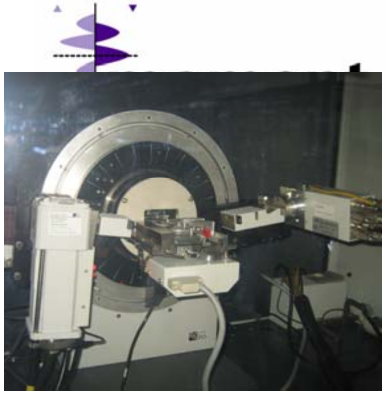
MPI-Chemie, Mainz

Universität Paderborn

- My background
- FeSe
  - Stoichiometry
  - Pressure
  - Doping
- Summary
- Interesting crystal structures

computational design

Rational Design

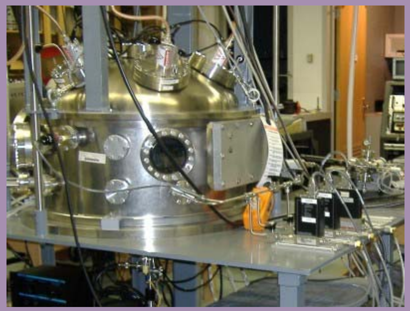


structure

Synthesis

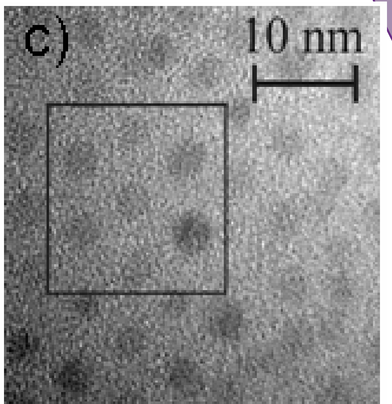
nano particles

single crystals

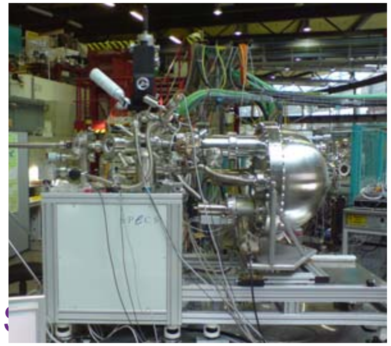


thin films

ceramics

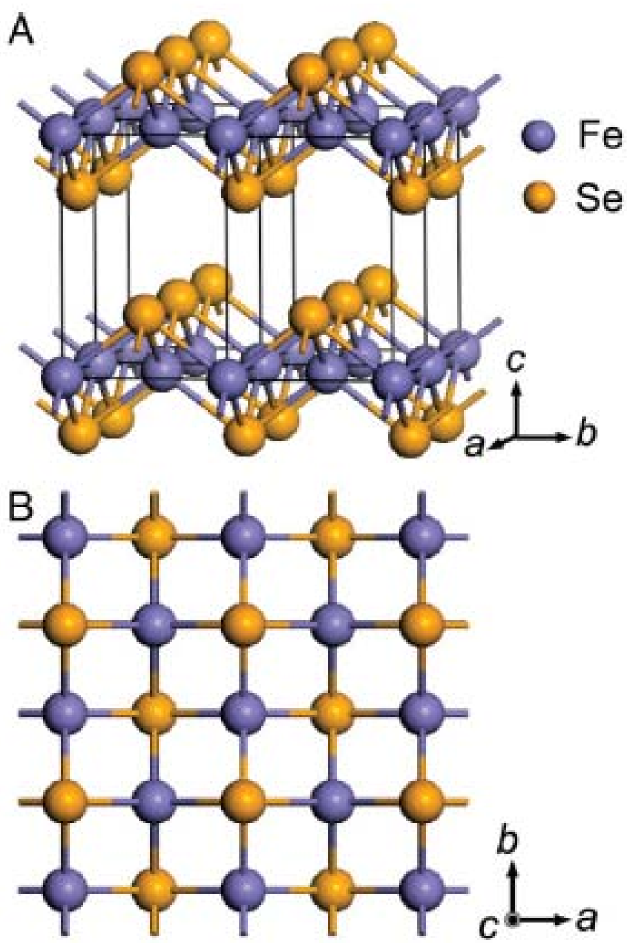


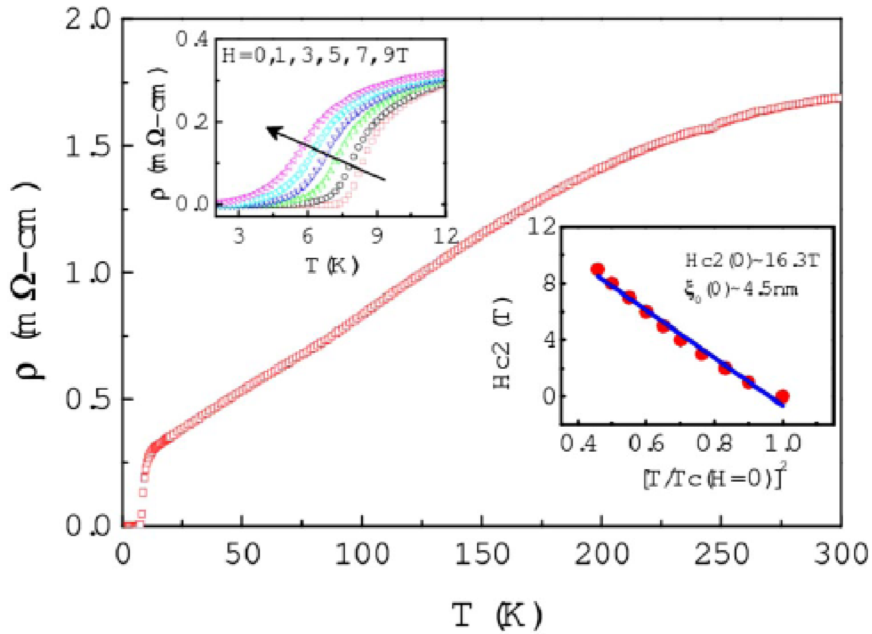
spectroscopy



Superconductivity in the PbO-type structure α-FeSe

Fong-Chi Hsu*†, Jiu-Yong Luo*, Kuo-Wei Yeh*, Ta-Kun Chen*, Tzu-Wen Huang*, Phillip M. Wu‡, Yong-Chi Lee*, Yi-Lin Huang*, Yan-Yi Chu*†, Der-Chung Yan*, and Maw-Kuen Wu*§





The estimated upper critical field Hc2 (0) is ~ 16.3 T, which gives a coherence length ξ_0 ~ 4.5 nm.

PNAS | September 23, 2008 | vol. 105 | no. 38 | 14263

Superconductivity in the PbO-type structure α-FeSe

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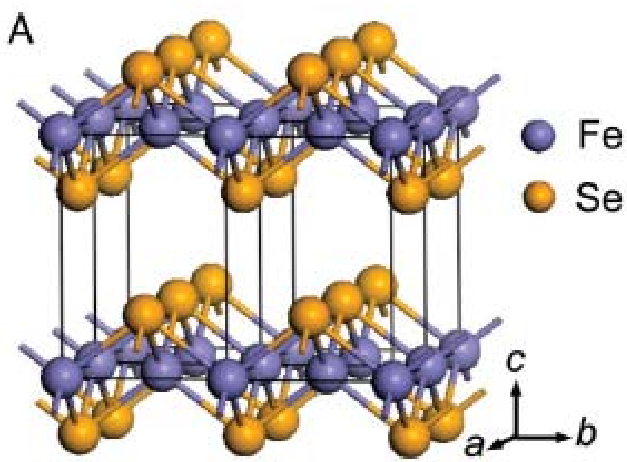

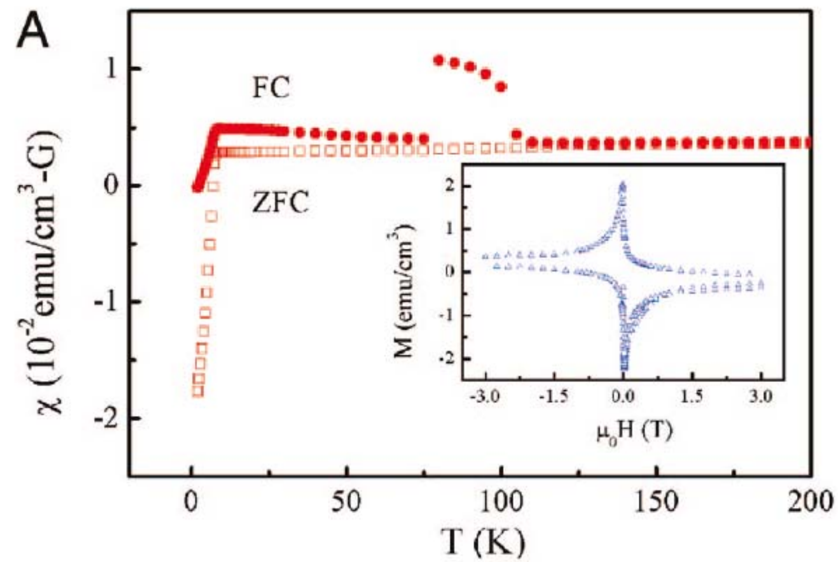

A key observation is that the clean superconducting phase exists only in those samples prepared with intentional Se deficiency.

- A small magnetic anomaly is observed at 105 K, which is more pronounced in the FC measurements.
- *Inset* shows the magnetic hysteresis of the sample measured at 2 K. It confirms the superconducting characteristic of the sample.

PNAS | September 23, 2008 | vol. 105 | no. 38 | 14263

Physica C 469 (2009) 340–349

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/physc

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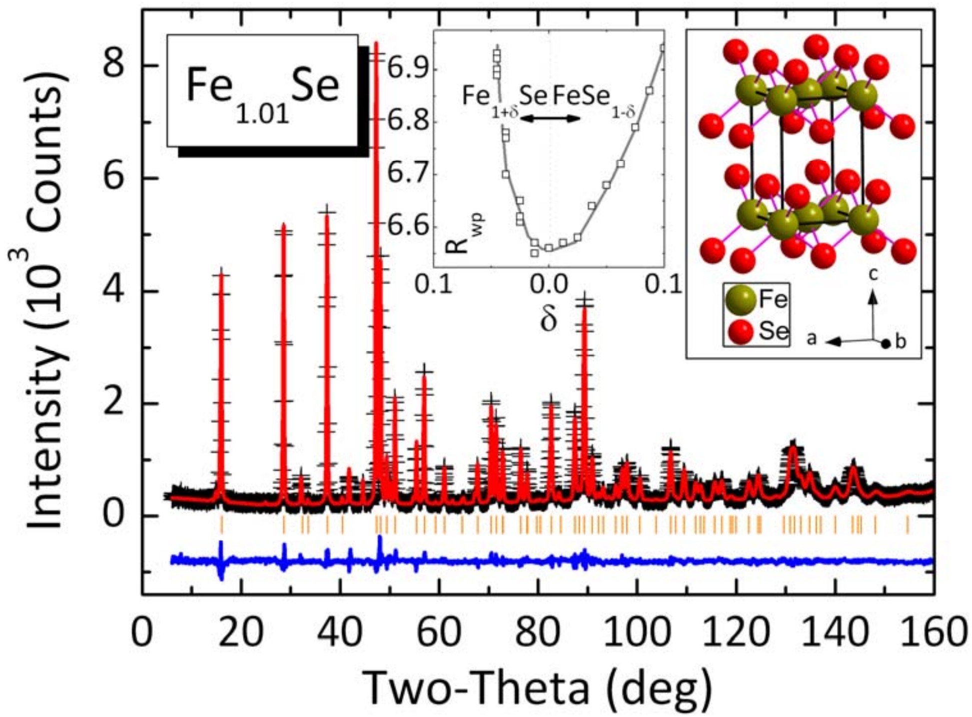
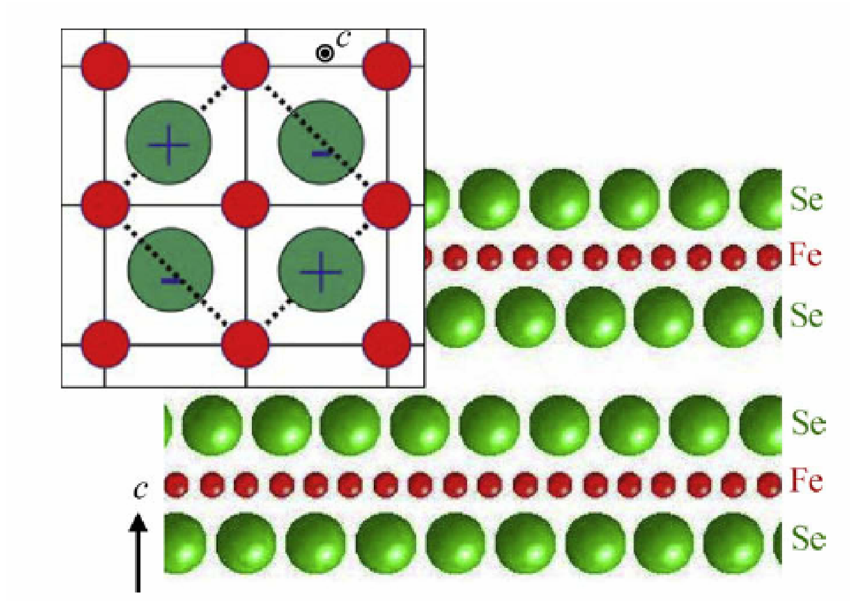
The development of the superconducting PbO-type β-FeSe and related compounds

M.K. Wu [a,b,*], F.C. Hsu [c,d], K.W. Yeh [a], T.W. Huang [a], J.Y. Luo [a], M.J. Wang [c], H.H. Chang [b], T.K. Chen [a], S.M. Rao [a], B.H. Mok [d], C.L. Chen [a], Y.L. Huang [a], C.T. Ke [a], P.M. Wu [e], A.M. Chang [e], C.T. Wu [b], T.P. Perng [d]

[a] Institute of Physics, Academia Sinica, Nankang, Taipei 115, Taiwan
[b] Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan
[c] Institute of Astrophysics and Astronomy, Academia Sinica, Taipei 115, Taiwan
[d] Department of Material Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan
[e] Department of Physics, Duke University, Durham, NC 27708, USA

$Fe_{1.01\pm0.2}Se$





D.J. Singh / Physica C 469 (2009) 418–424

Superconductivity depends strongly on the stoichiometry

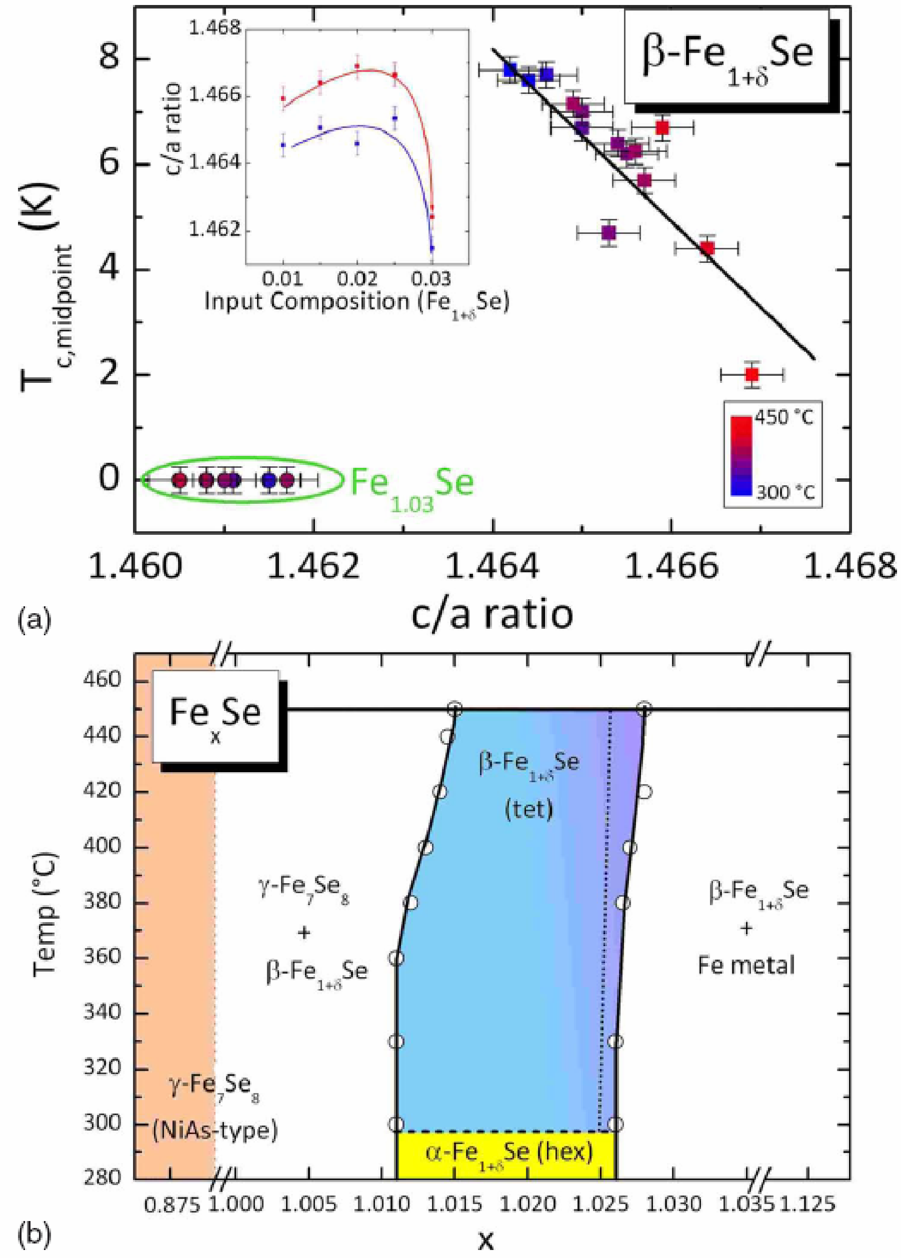
100% superconducting sample for $Fe_{1.01\pm0.2}Se$

Excess Fe instead of Se deficiency

McQueen et al. Phys. Rev. B **79** (2009) 014522

$Fe_{1.01}Se$

- Freshly polished iron pieces and selenium shot
- Sealed in silica tubes under vacuum with a piece of cleaned carbon
- Sealed in a second evacuated silica ampoule
- Complex annealing procedure
- Small pieces were then loaded into small silica ampoules and annealed at various temperatures 300–500 °C or 2 days followed by quenching in −13 °C brine. Protection from oxidation in air by storage in an argon glove box.

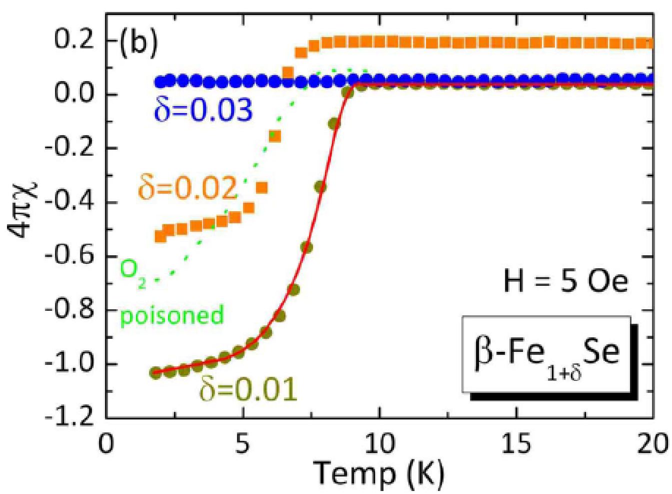


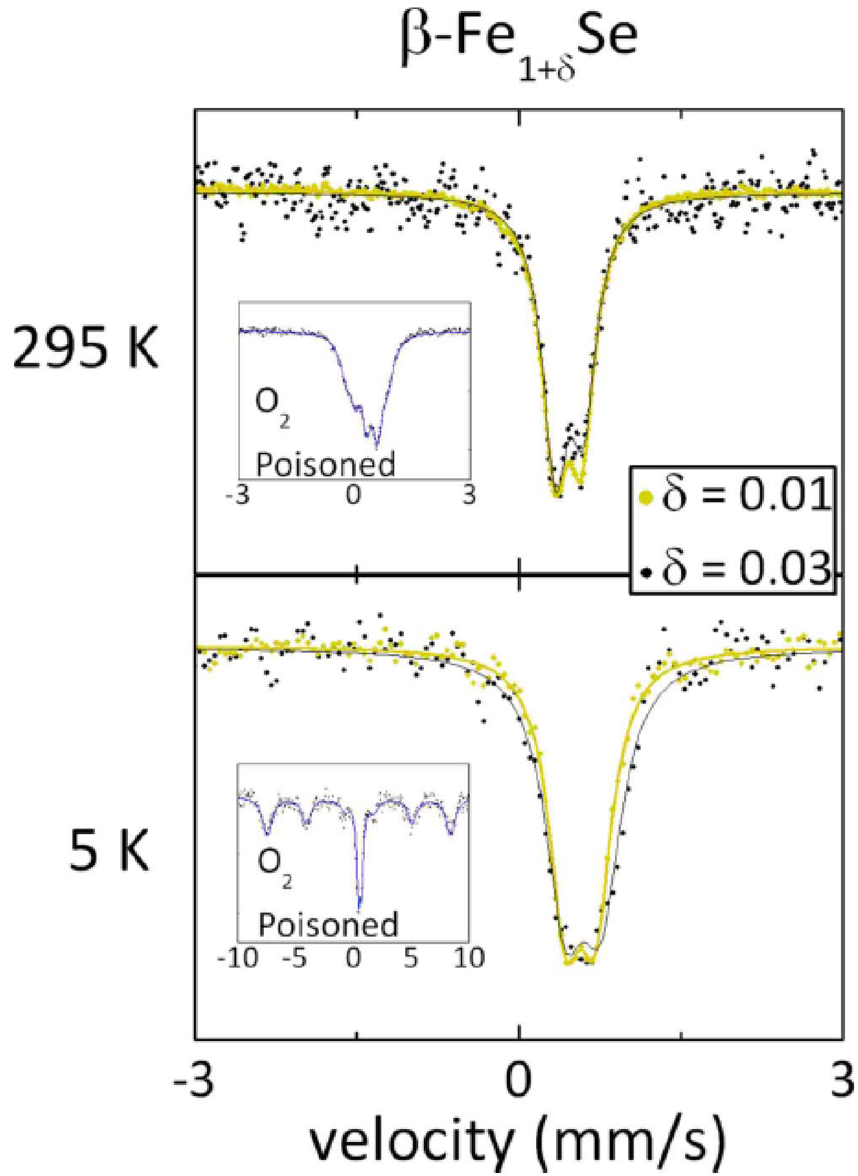
McQueen et al. Phys. Rev. B **79** (2009) 014522

moment

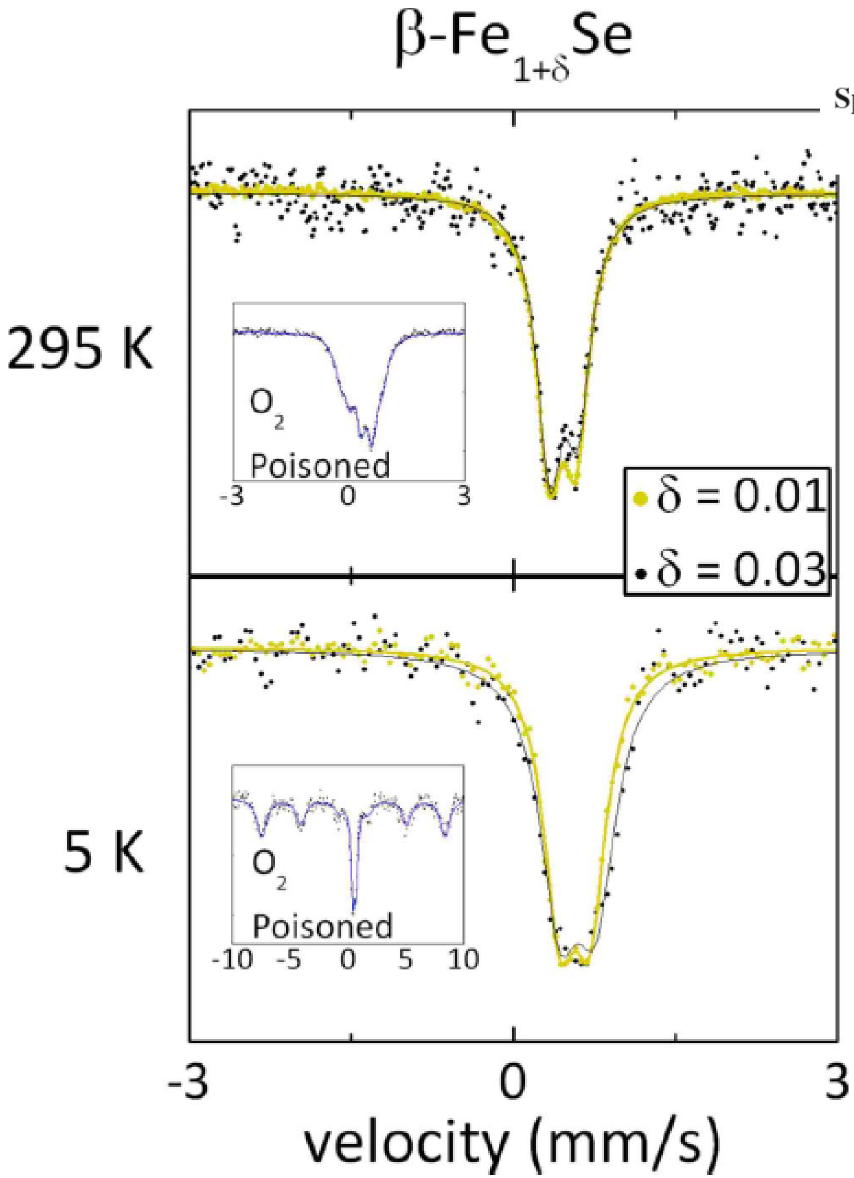
$Fe_{1.01}Se$

- No long range magnetic interaction in superconduct $Fe_{1.01}Se$
- No long range magnetic interaction in non superconducting $Fe_{1.03}Se$
- Impurities suppress superconductivity





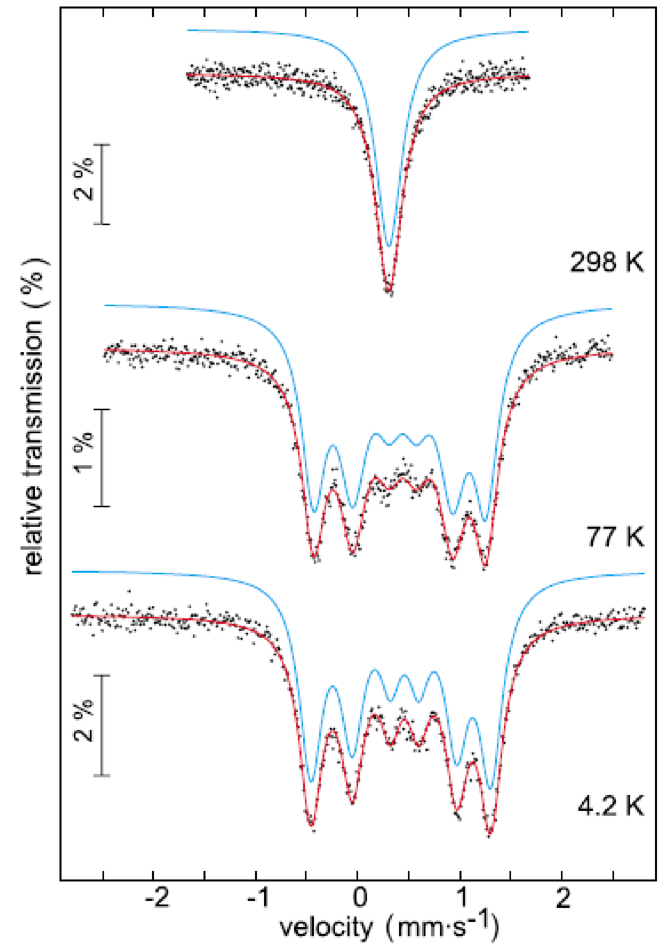
$Fe_{1.01}Se$



PHYSICAL REVIEW B **78**, 020503(R) (2008)

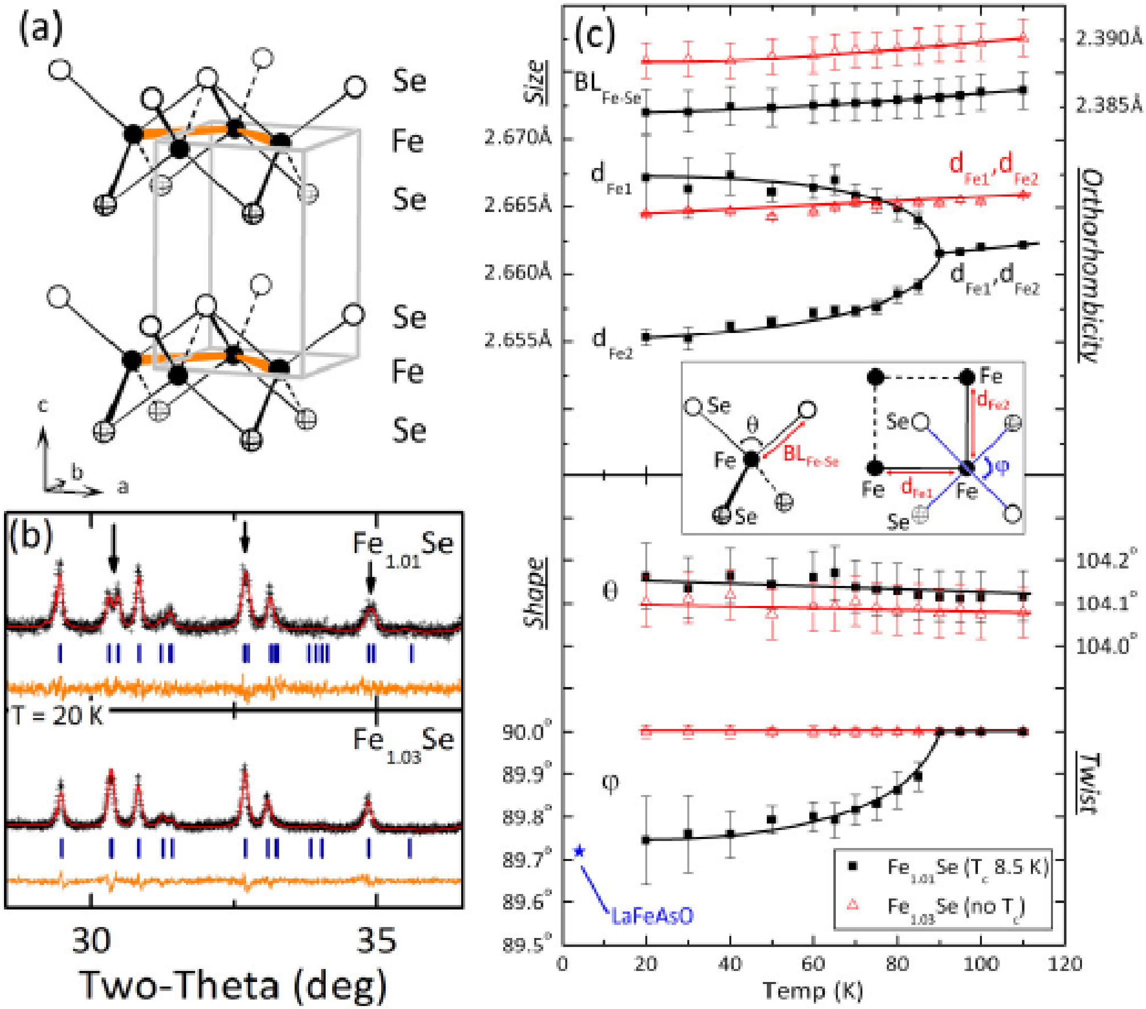
Spin-density-wave anomaly at 140 K in the ternary iron arsenide $BaFe_2As_2$

Marianne Rotter, Marcus Tegel, and Dirk Johrendt*



McQueen et al. Phys. Rev. B **79** (2009) 014522

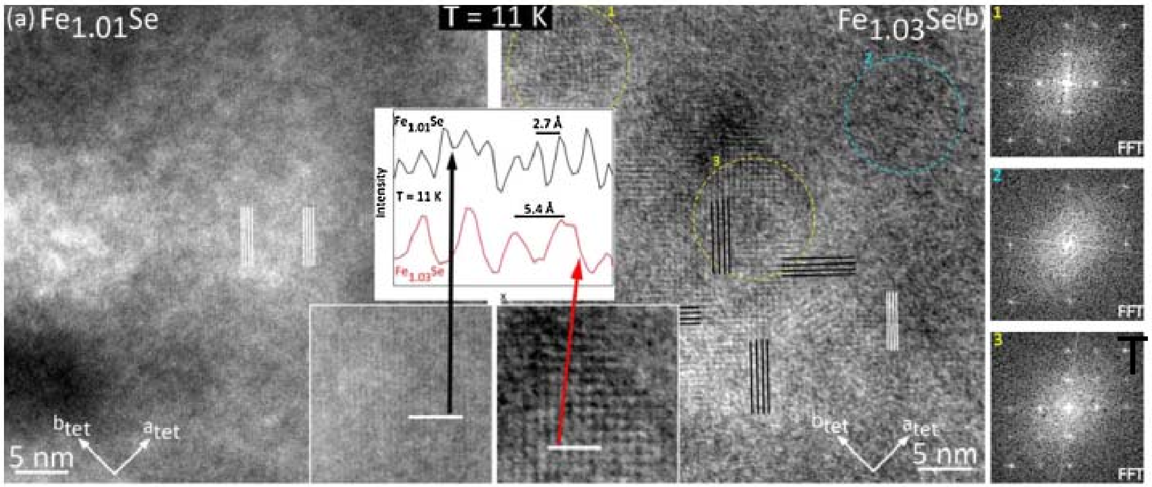
$Fe_{1.01}Se$ below 100 K: dimer formation

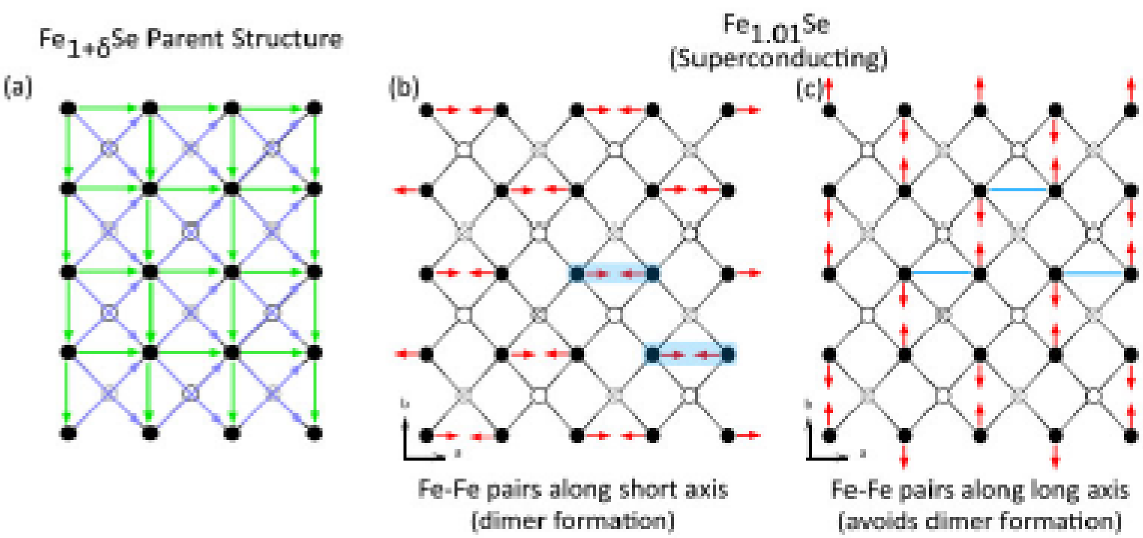


- On cooling, $Fe_{1.01}Se$ undergoes a twisting of the tetrahedra, splitting the Fe-Fe distances into two distinct sets.
- Nonsuperconducting $Fe_{1.03}Se$, in contrast, shows no transition by XRD.

McQueen et al., Phys. Rev. Lett 103 057002 (2009).

$Fe_{1.01}Se$ below 100 K: dimer formation

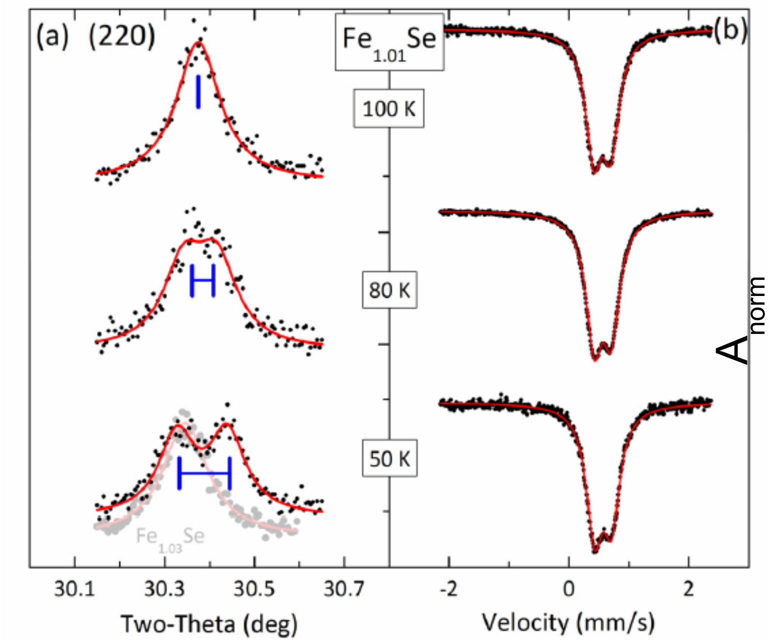


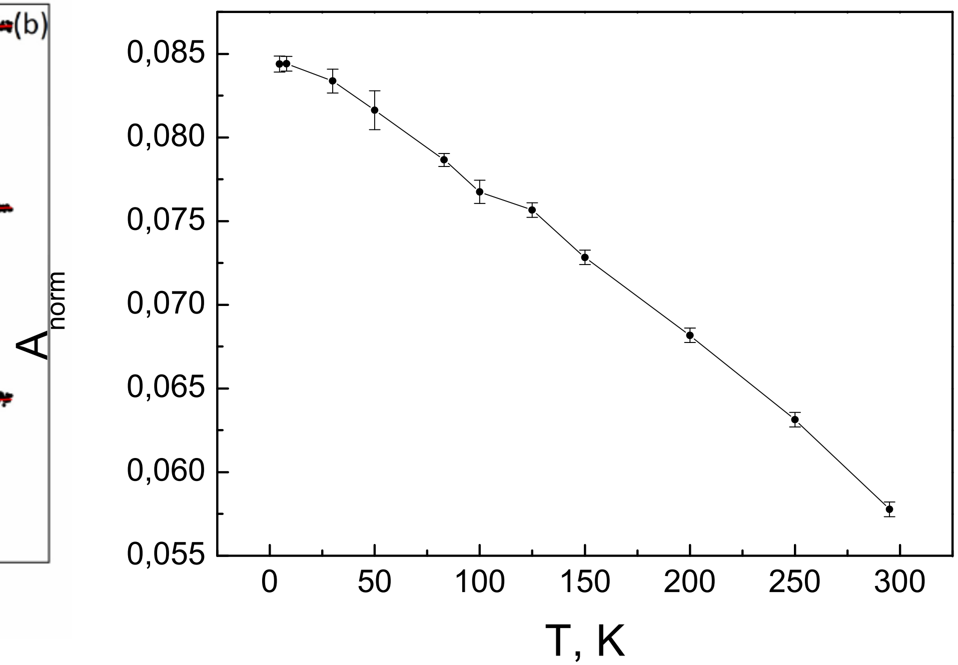


The first is by displacement of pairs of iron ions along the short in-plane a-axis. This is consistent with the formation of Fe-Fe dimers, which would imply that the transition is driven by an increase in metal-metal bonding.

McQueen et al., Phys. Rev. Lett 103 057002 (2009).

Tetra-Ortho transition in $Fe_{1.01}Se$ below 100 K





Normalized area under Mössbauer spectra is sensitive to the tetra- ortho transition.

Ortho phase is more soft

The non superconducting phases are less soft

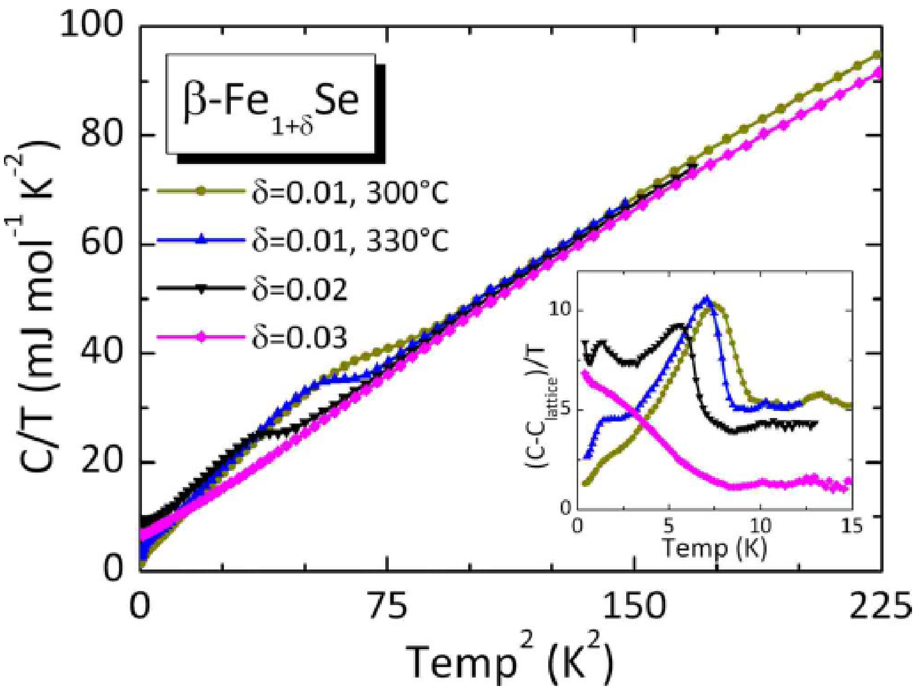
Dependence of the Mössbauer-Lamb factor from the properties

$Fe_{1.01}Se$	$f = 0.11(1)$
$Fe_{1.03}Se$	$f = 0.16(1)$
$Fe_{0.97}Cu_{0.04}Se$	$f = 0.18(1)$

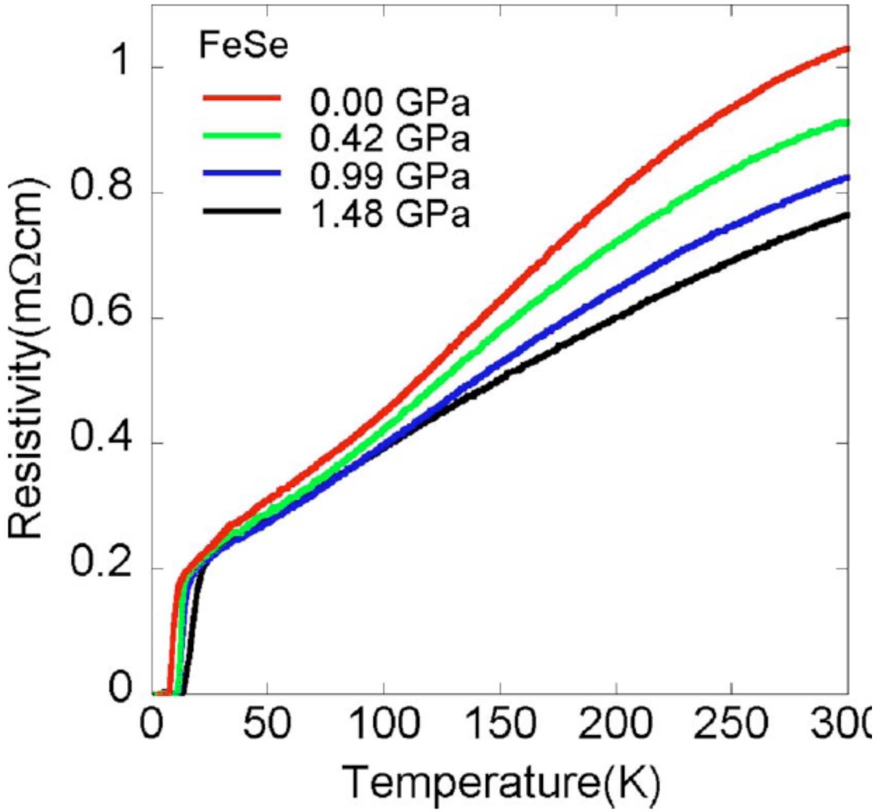
McQueen et al., Phys. Rev. Lett (2009).

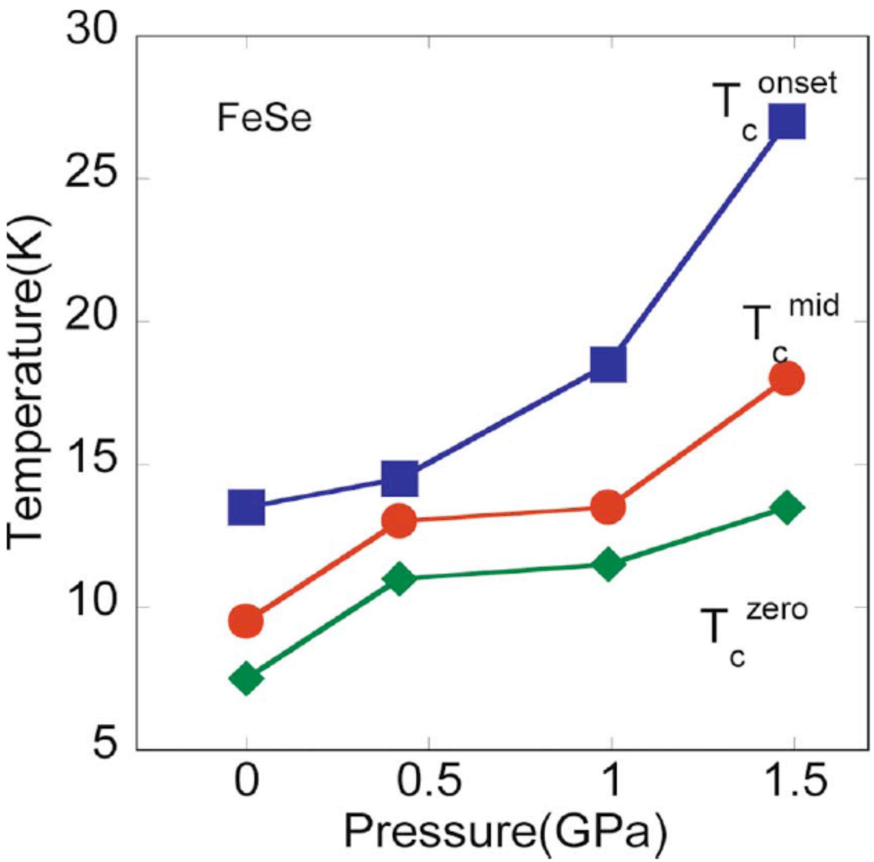
$Fe_{1.01}Se$

- Estimation of the normalized specific-heat jump at *Tc* is *C*/*Tc*=1.31, which is in good agreement with the BCS expected value of 1.4.
- This confirms the bulk nature of the superconductivity below 8.5 K in $Fe_{1.01}$Se-300 °C.
- There is a second transition at 1K in the superconducting sample



FeSe: superconductivity under pressure



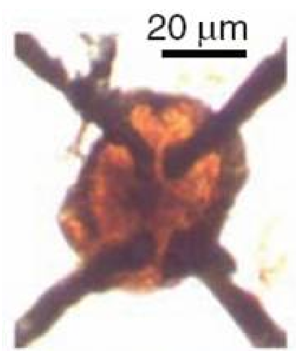


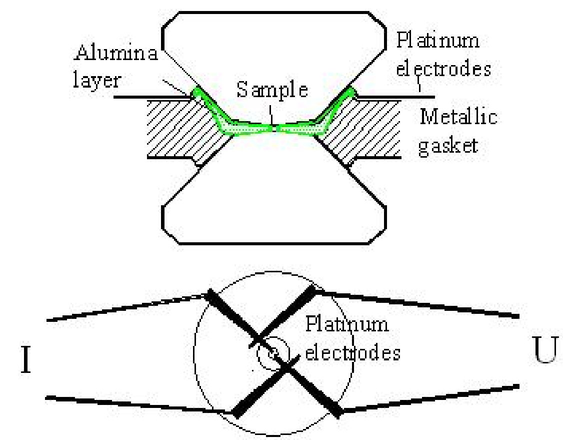
Y. Mizuguchi, et al Appl. Phys. Lett. 93, 152505 2008

LETTERS
PUBLISHED ONLINE: 14 JUNE 2009 | DOI: 10.1038/NMAT2491
nature materials

Electronic and magnetic phase diagram of β-$Fe_{1.01}Se$ with superconductivity at 36.7 K under pressure

S. Medvedev[1,2], T. M. McQueen[3], I. A. Troyan[2,4], T. Palasyuk[2,5], M. I. Eremets[2], R. J. Cava[3], S. Naghavi[1], F. Casper[1], V. Ksenofontov[1], G. Wortmann[6] and C. Felser[1]*

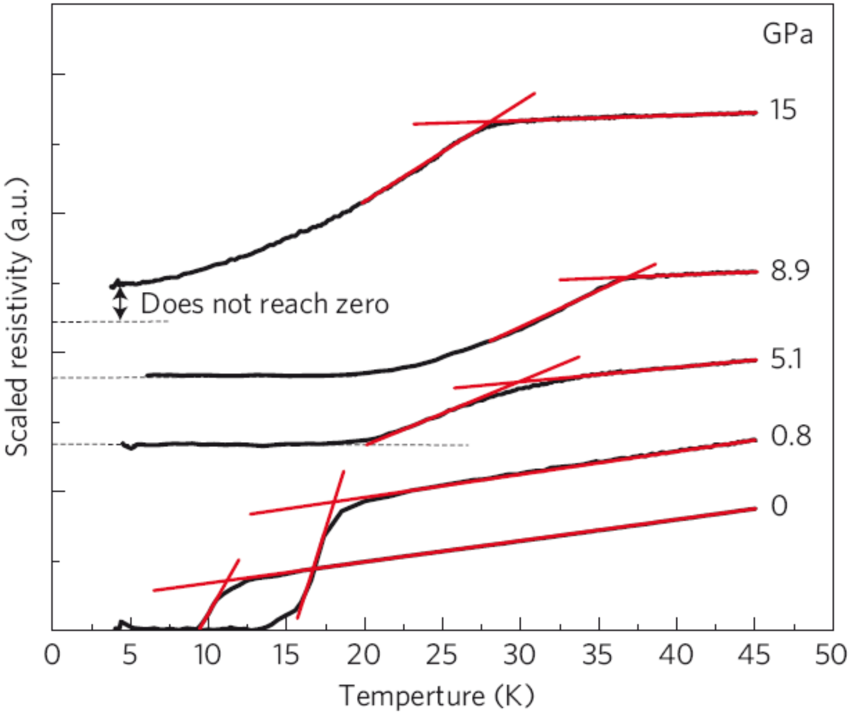


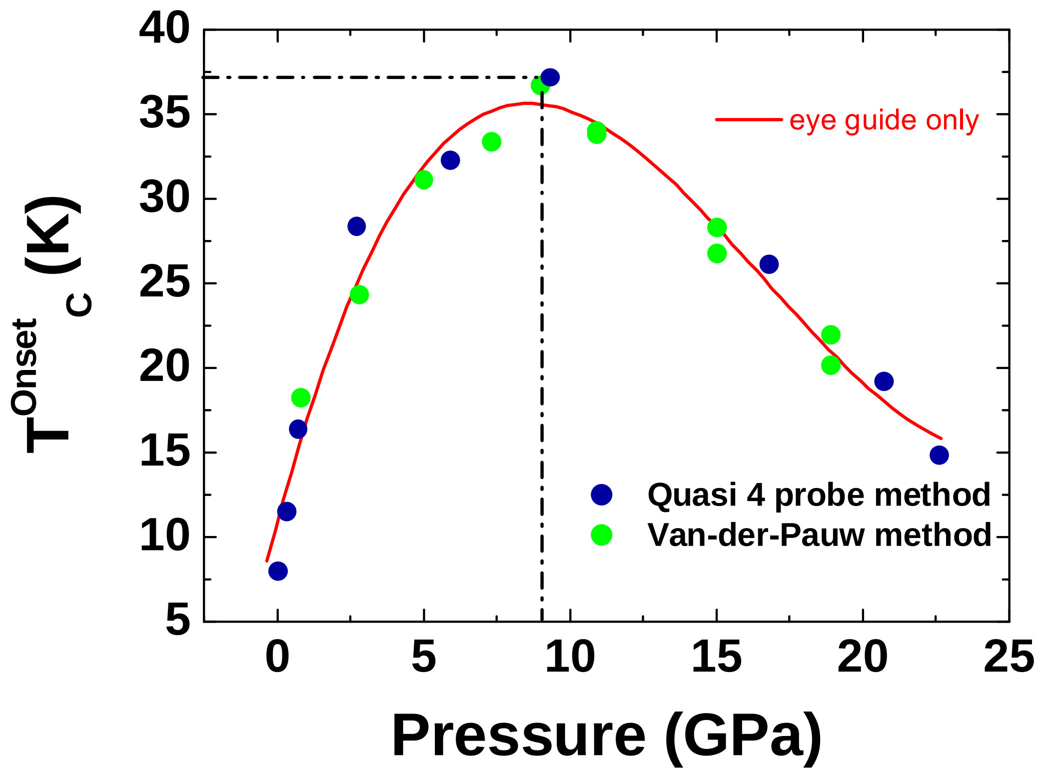


M. I. Eremets, *et al.*, *Science* **319**, 1506 (2008)

Medvedev et al. Nat. Mat. 8 630 (2009) arXiv:0903.2143

$Fe_{1.01}Se$ under pressure: Transport

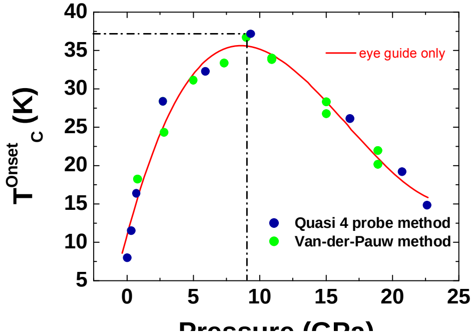




- Maximum of T_C: 37 K at 8.9 GPa

Medvedev et al. Nat. Mat. 8 630 (2009) arXiv:0903.2143

$Fe_{1.01}Se$ under pressure: Transport

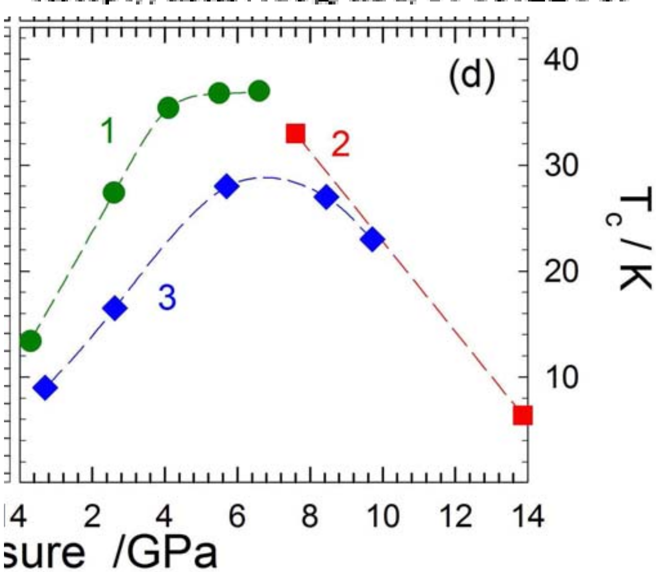


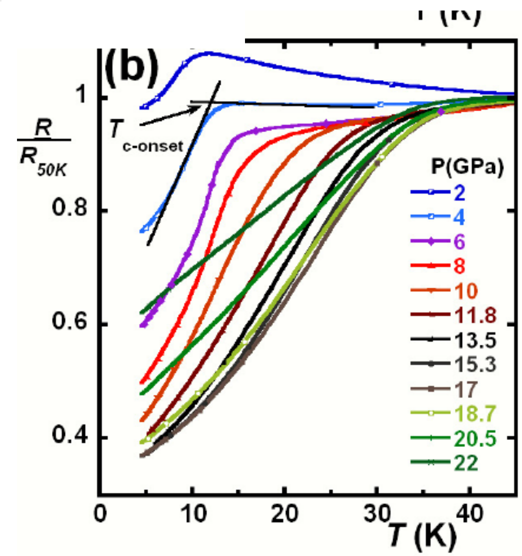
EPL, **86** (2009) 27001
doi: 10.1209/0295-5075/86/27001
www.epl

High-temperature superconductivity (T_c onset at 34 K) in the high-pressure orthorhombic phase of FeSe

G. Garbarino[1(a)], A. Sow[2], P. Lejay[2], A. Sulpice[2], P. Toulemonde[2], M. Mezouar[1] and M. Núñez-Regueiro[2]

Margadonna, S. *et al.* Pressure evolution of low-temperature crystal structure and bonding of 37 K T_cFeSe superconductor. Preprint at <http://arxiv.org/abs/0903.2204> (2009).

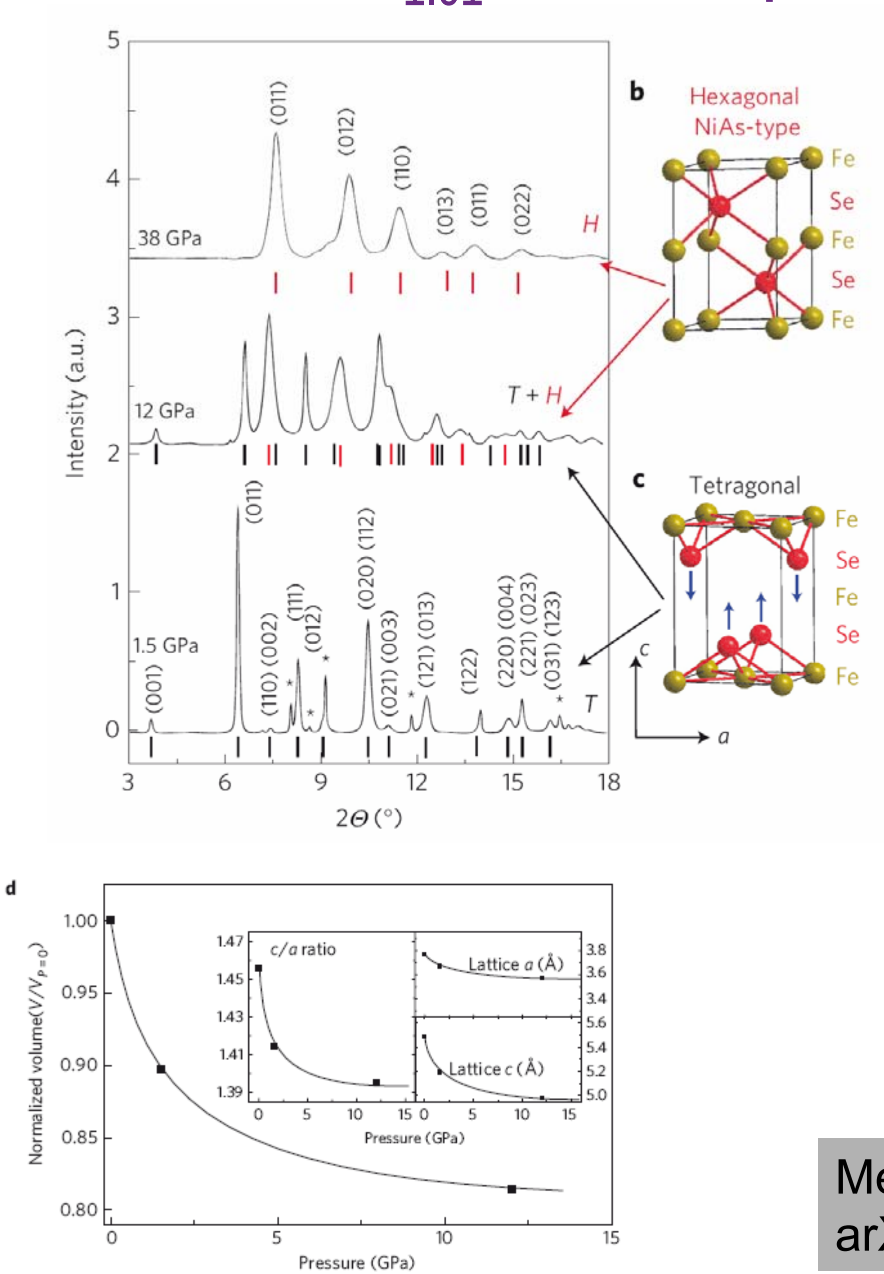




- Confirmed by other groups

Medvedev et al. Nat. Mat. 8 630 (2009) arXiv:0903.2143

$Fe_{1.01}Se$ under pressure: Structure



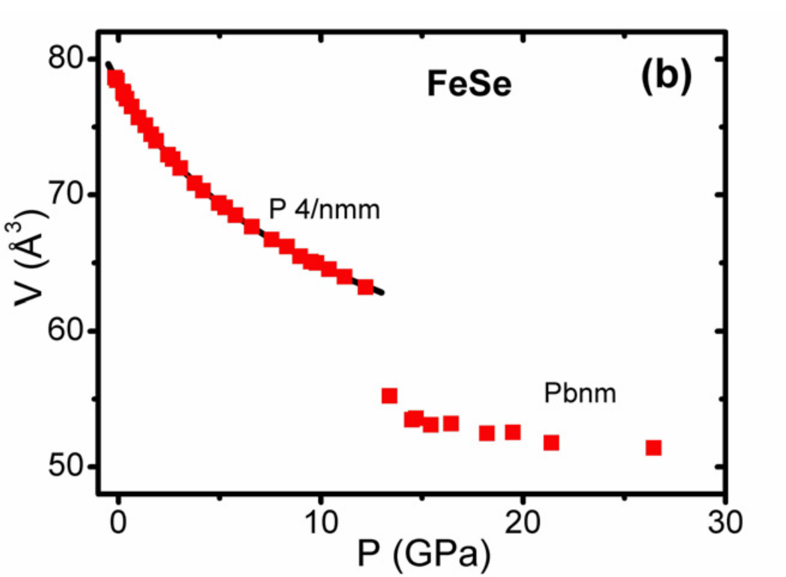
- Superconductivity depends strongly on the stoichiometry
- Very soft material
- Transforms under pressure into the NiAs type structure

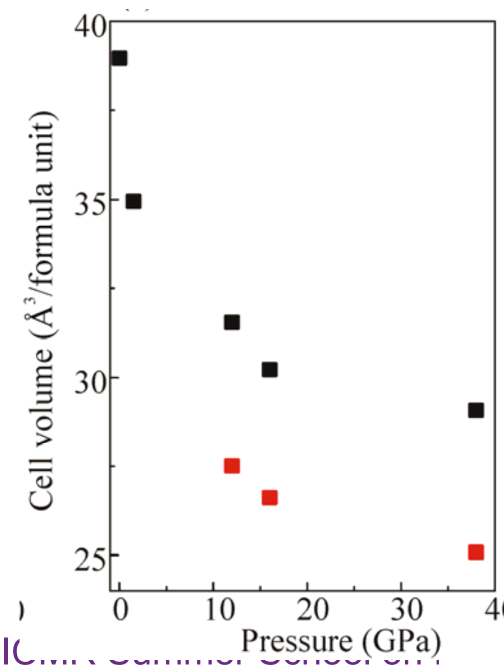
- Struture determinations were done at
  - •ESRF
  - •Taiwan
  - •SPring8

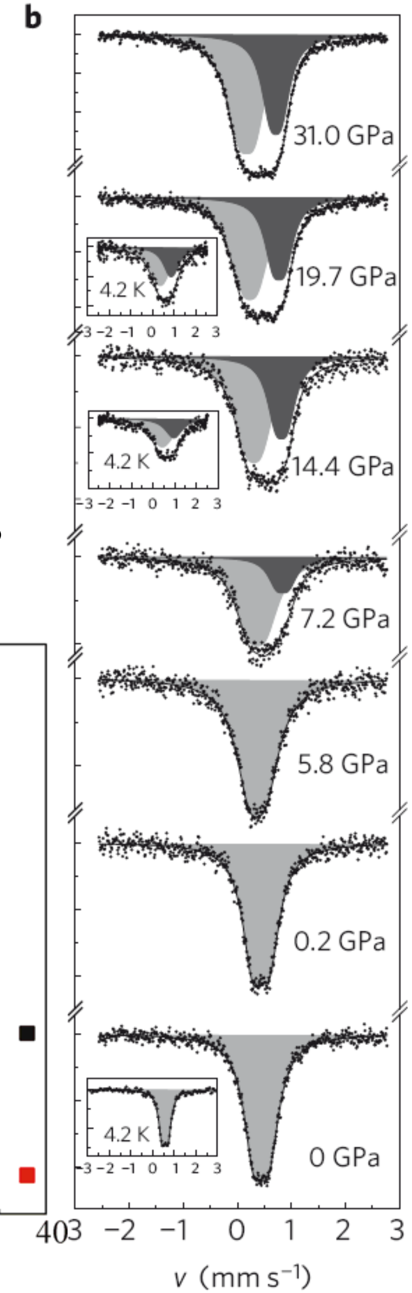
Medvedev et al. Nat. Mat. 8 630 (2009)
arXiv:0903.2143

$Fe_{1.01}Se$

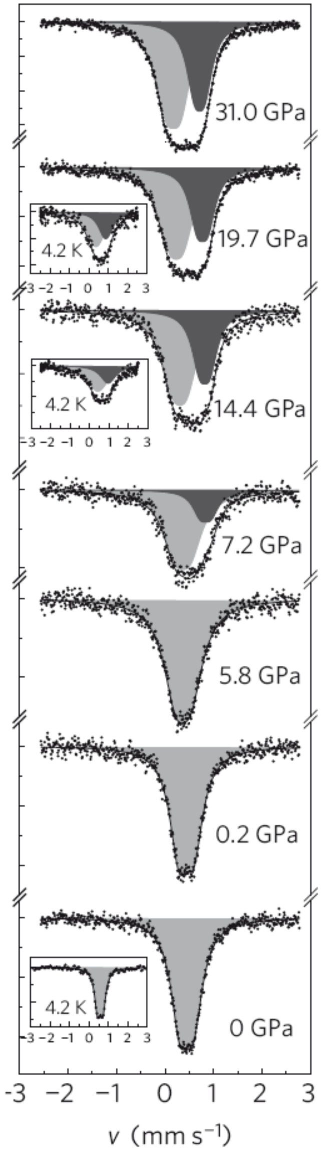
- Limitation of superconductivity related to the tetragonal phase (black) by the appearance of the hexagonal more dense semiconducting phase (red)
- Nicely seen also in the Mößbauerspectra: the isomer shift of the tetragonal covalent FeSe is smaller compared to the hexagonal FeSe
- The hexagonal FeSe exists under ambient conditions only off stochiometric and is magnetic
- The transition is reversible

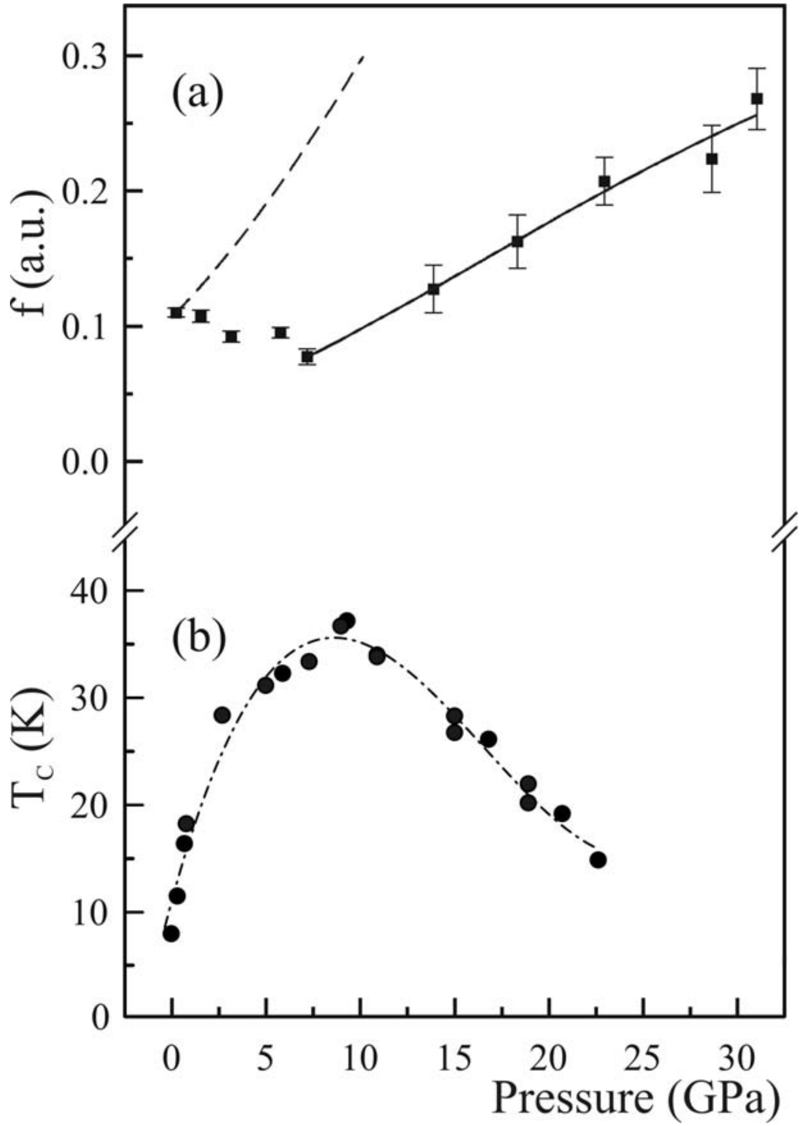






$Fe_{1.01}Se$

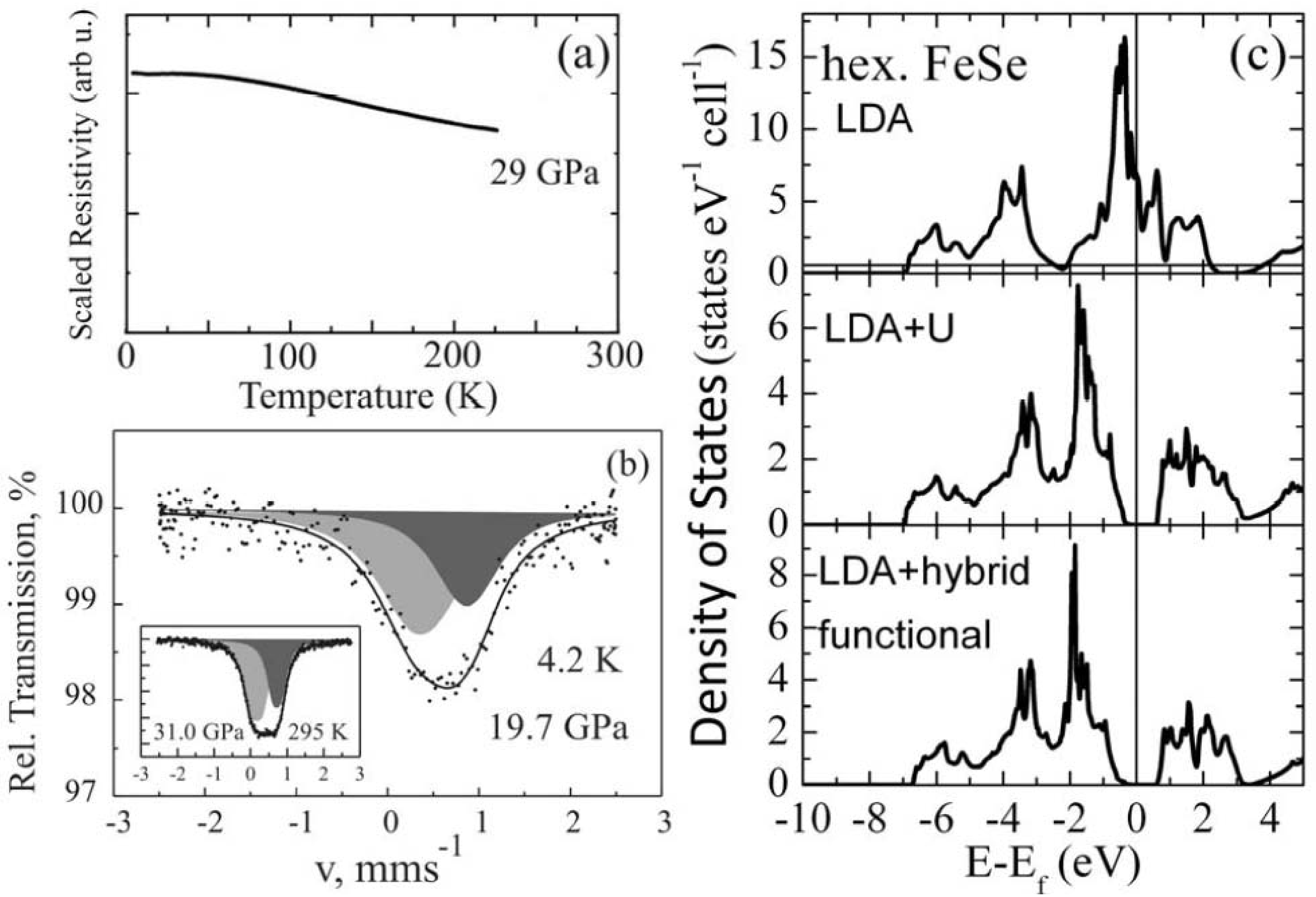




- Anomalous p-dependence of the Debye Waller factor
- Phonon softening observed for the superconducting phase
- Limited by the appearance of the hexagonal phase
- Electron phonon coupling might be also important

Ksenofontov et al. To be published

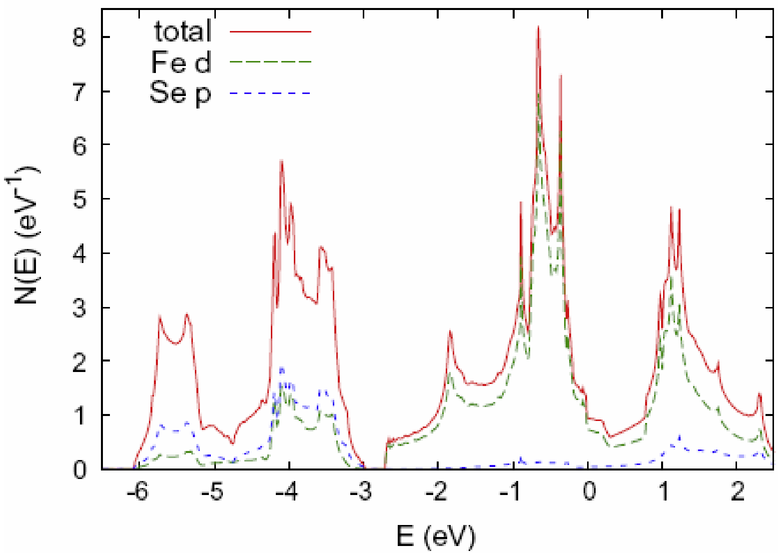
Hexagonal $Fe_{1.01}Se$



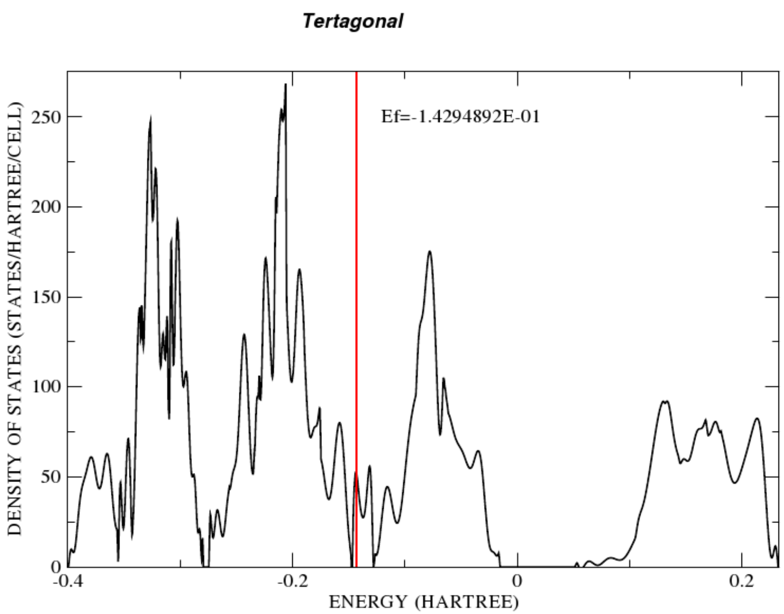
Semiconducting ground state of the NiAs phase can not described within the LSDA

Medvedev et al. Nat. Mat. 8 630 (2009) arXiv:0903.2143

Tetragonal FeSe



D.J. Singh / Physica C 469 (2009) 418–424

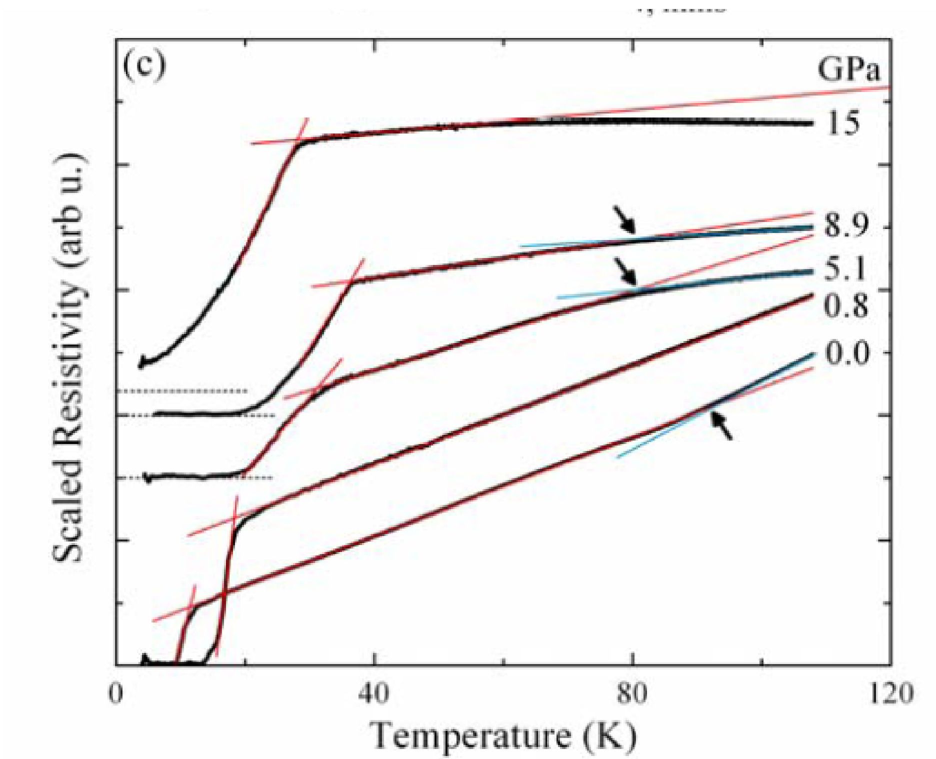


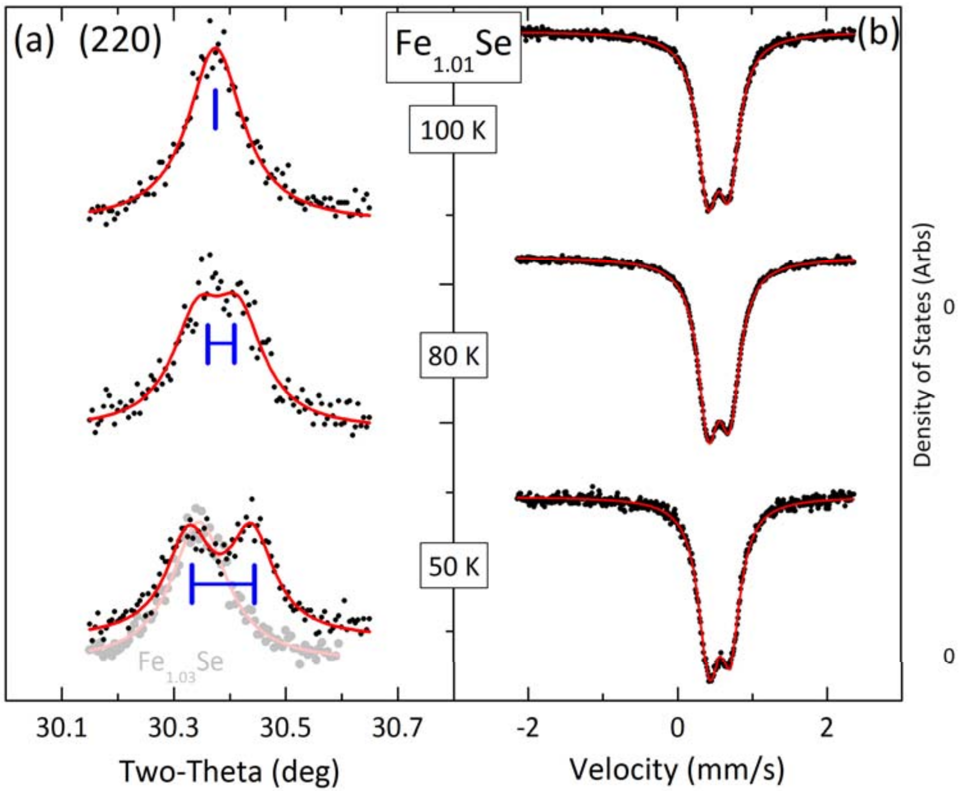
Shahab Naghavi with Crystal06 and Hybridfunctional

$Fe_{1.01}Se$

Tetragonal to orthorhombic transition ~100K only in the superconducting phase

Linear resistance of the orthorhombic phase: anomalous metal?



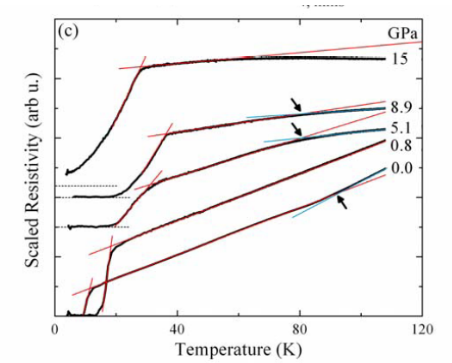


Medvedev et al. Nat. Mat. 8 630 (2009) arXiv:0903.2143

McQueen et al. PRL 103, 057002 arXiv:0905.1065v1 (2009).

$Fe_{1.01}Se$: evidence for quantum critcality

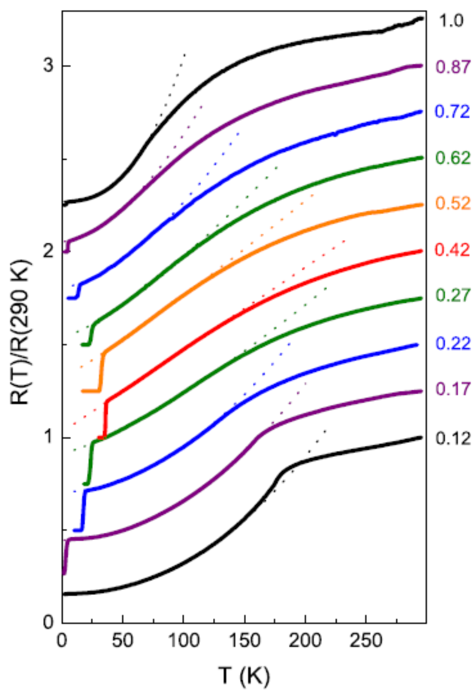
moment



PHYSICAL REVIEW B **79**, 104504 (2009)

Evidence of quantum criticality in the phase diagram of $K_xSr_{1-x}Fe_2As_2$ from measurements of transport and thermoelectricity

Melissa Gooch,[1] Bing Lv,[2] Bernd Lorenz,[1] Arnold M. Guloy,[2] and Ching-Wu Chu[1,3,4]



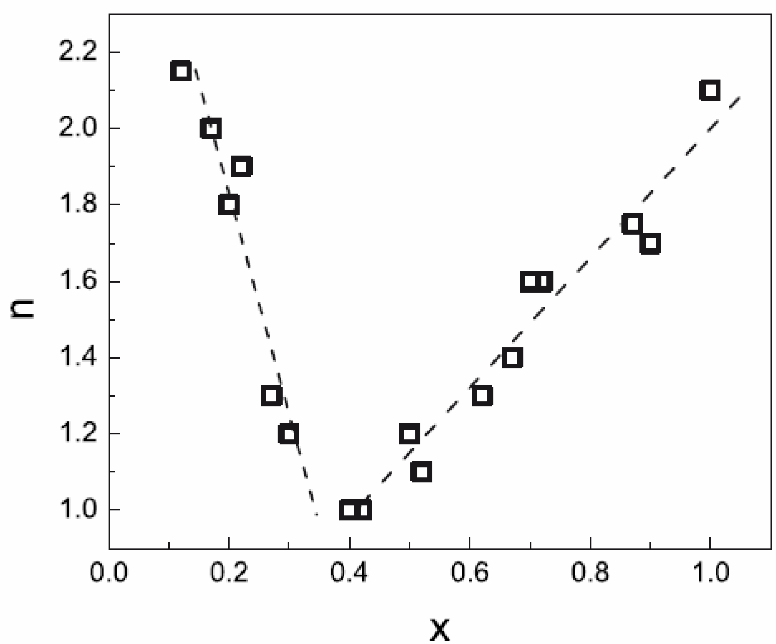
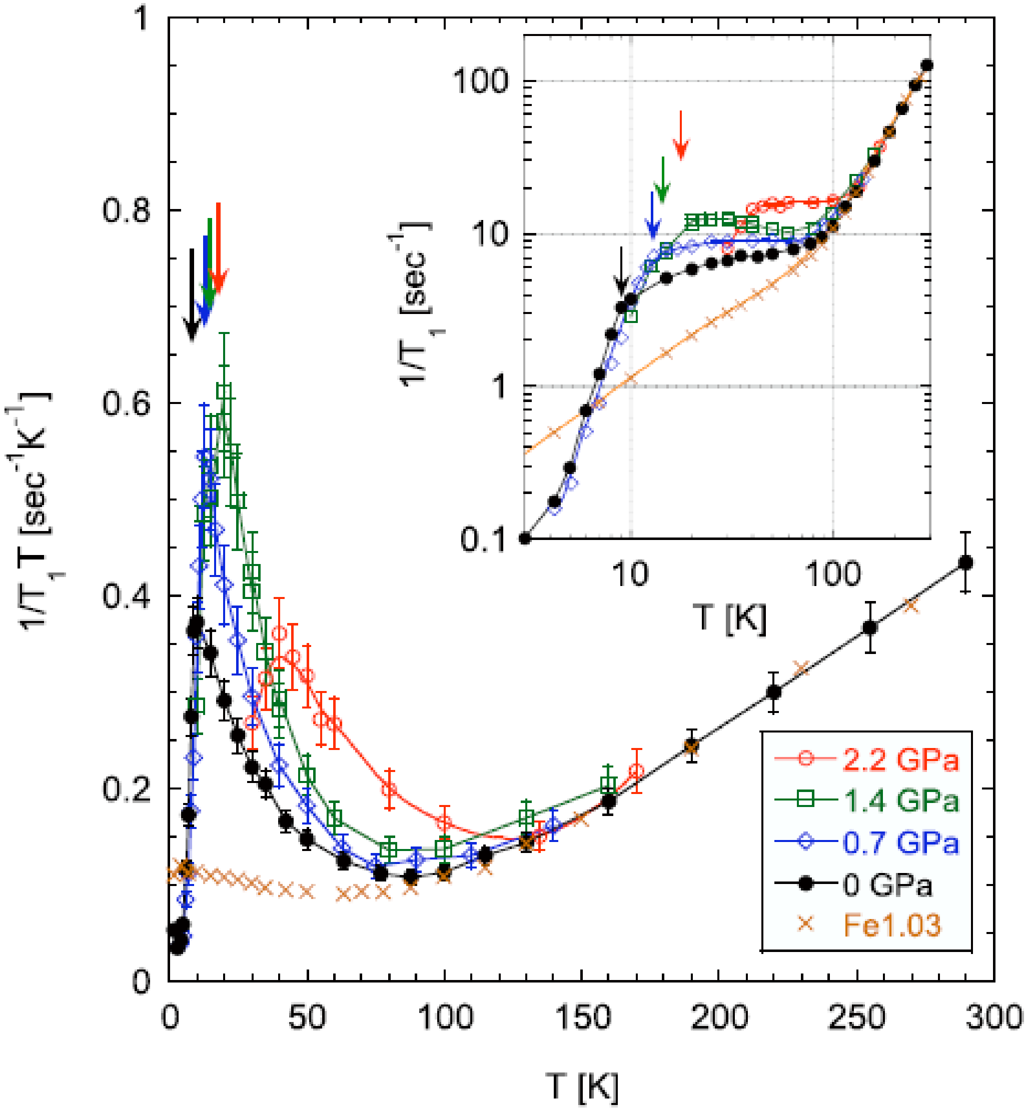


FIG. 3. The resistivity exponent n as a function of x.

$Fe_{1.01}Se$

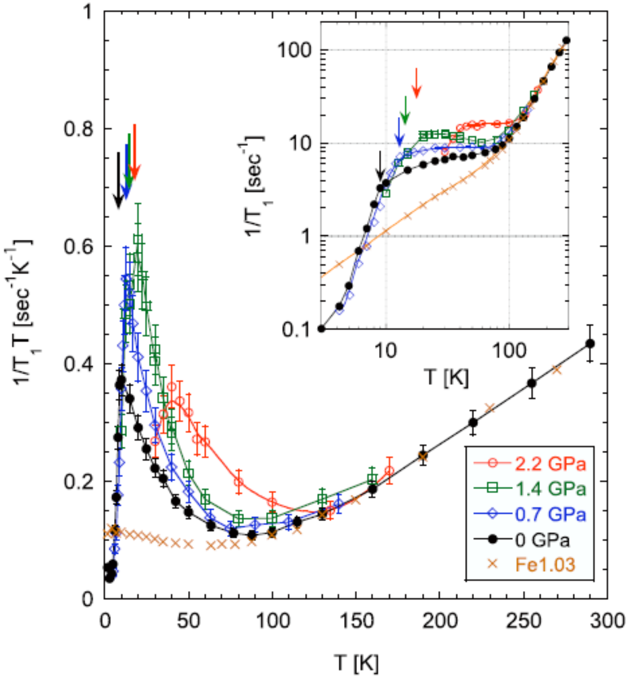


^{77}Se NMR spin-lattice relaxation rate, $1/T_1$:

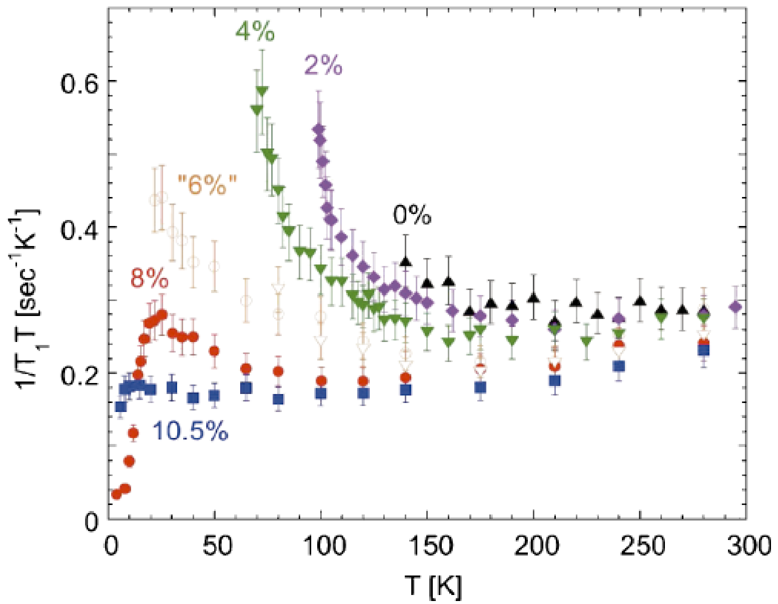
- Strong enhancement towards Tc of antiferromagnetic spin fluctuations
- Hydrostatic pressure enhances spin fluctuations as well as Tc.
- Electronic properties of FeSe are very similar to those of electron-doped FeAs superconductors,

T. Imai et al. PRL 102, 177005 (2009)

$Fe_{1.01}Se$



As NMR lineshapes for $Ba(Fe_{1-x}Co_x)_2As_2$

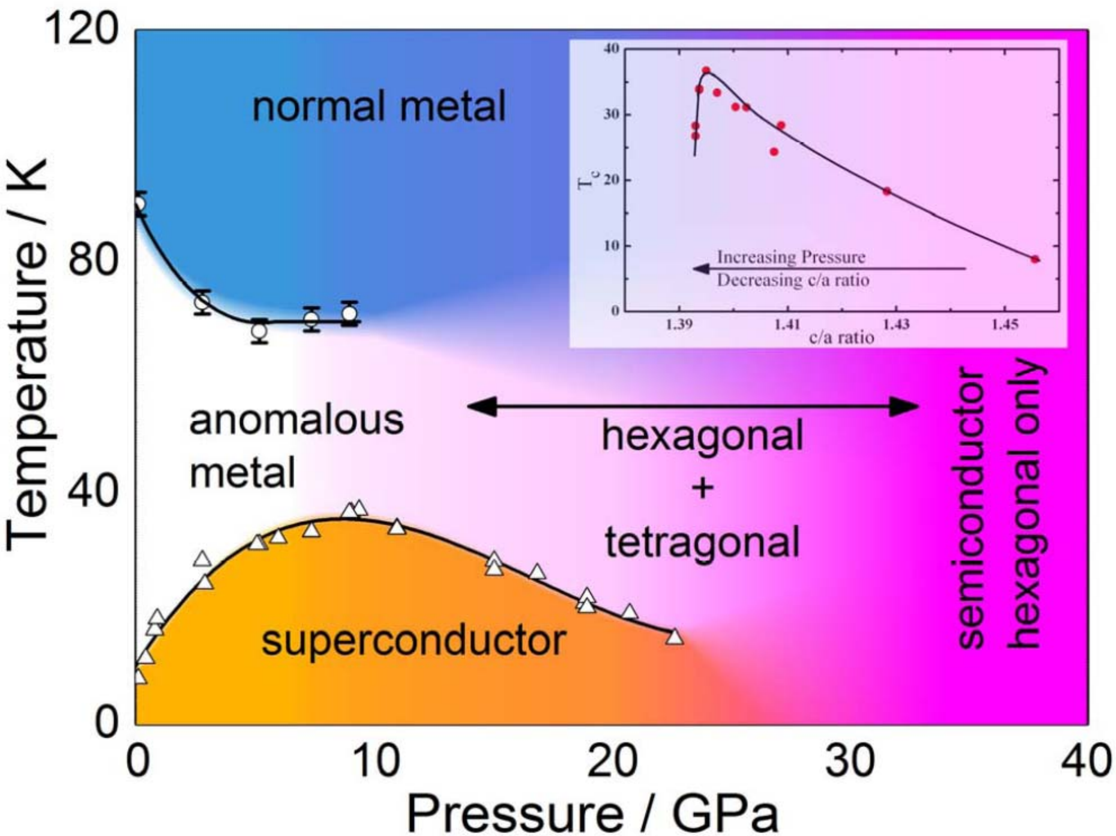


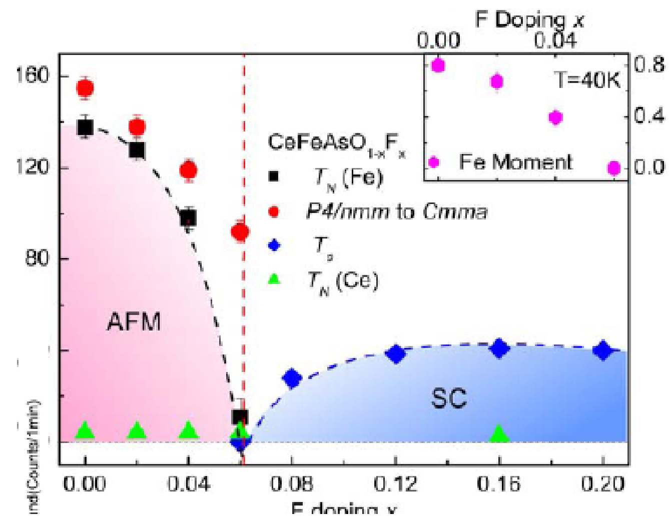
This finding suggests that undoped FeSe superconductor is actually on the verge of an SDW ordering.

91) F. L. Ning, K. Ahilan, T. Imai, A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, and D. Mandrus: J. Phys. Soc. Jpn. 77 (2008) 103705.
92) F. L. Ning, K. Ahilan, T. Imai, A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, and D. Mandrus: J. Phys. Soc. Jpn. 78 (2009) 013711.

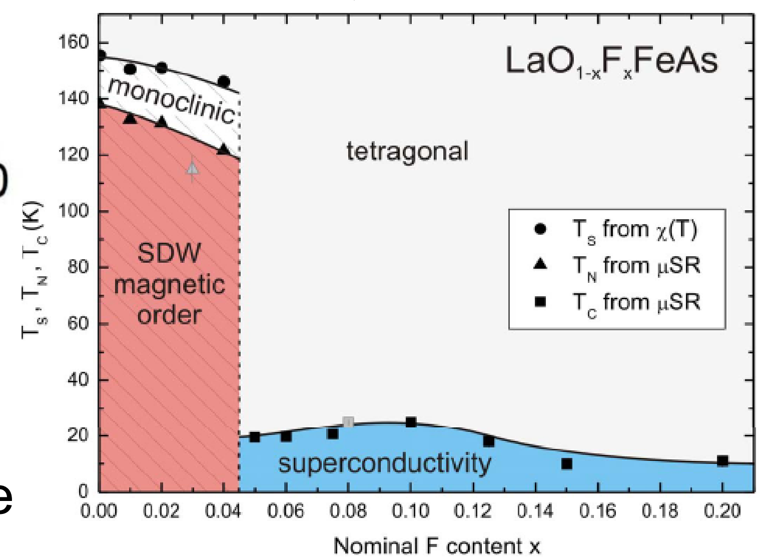
T. Imai et al. PRL 102, 177005 (2009)

The Phase diagram of $Fe_{1.01}Se$





Zhao et al., arXiv:0806.2528



- Structural phase transition above T_C
- No spin density wave instability
- Reversible phase transition: NiAs structure

Medvedev et al. Nat. Mat. 8 630 (2009) arXiv:0903.2143

Doping of FeSe

Al, Ga, Sm occupies the Fe sites – no possitiv influence on the superconducting properties

Ti, V, Cr destroys superconductivity

Table 1
The superconducting transition, the phase transition temperatures and γ angle for FeSe/Te compounds.

	T_c	Phase transition temperature	γ angle[b] (°) at 6 K
$FeSe_{0.88}$	8.5 K	~105 K	90.279
FeTe	None	~80 K[a]	90
$Fe(Se_{0.5}Te_{0.5})$	15.2 K	~100 K	90.122
$(Fe_{0.9}Mn_{0.1})Se_{0.85}$	11.2 K	~85 K	90.166
$(Fe_{0.9}Cu_{0.1})Se_{0.85}$	None	None	90

[a] The FeTe phase transition is from high temperature tetragonal phase (P4/nmm) to an orthorhombic (Pmmn) symmetry.
[b] The γ angle is defined as an angle between a_T-and b_T axes in the original tetragonal unit cell.

The development of the superconducting PbO-type β-FeSe and related compounds

M.K. Wu[a,b,*], F.C. Hsu[c,d], K.W. Yeh[a], T.W. Huang[a], J.Y. Luo[a], M.J. Wang[c], H.H. Chang[b], T.K. Chen[a], S.M. Rao[a], B.H. Mok[d], C.L. Chen[a], Y.L. Huang[a], C.T. Ke[a], P.M. Wu[e], A.M. Chang[e], C.T. Wu[b], T.P. Perng[d]

Physica C 469 (2009) 340–349

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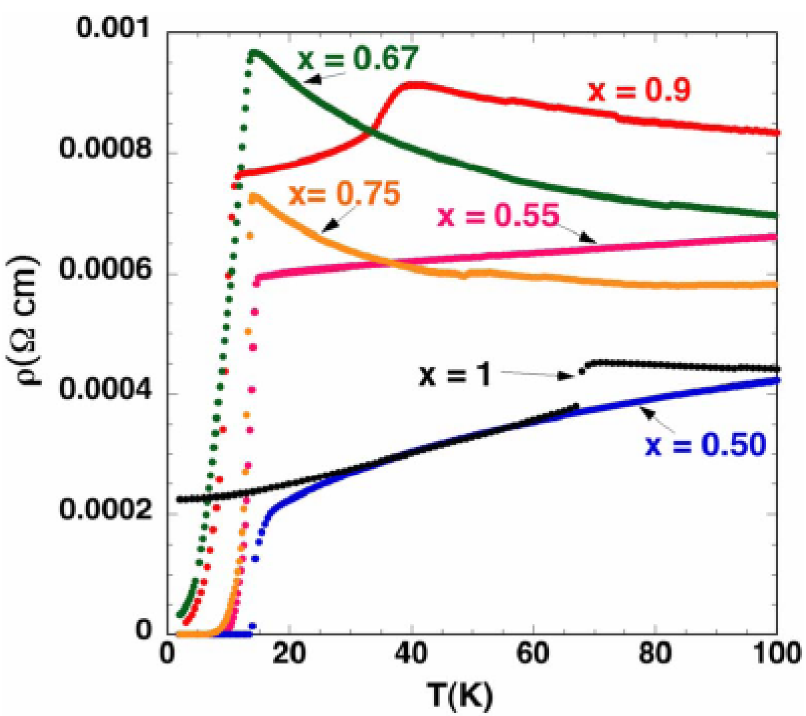
PHYSICAL REVIEW B **79**, 094521 (2009)

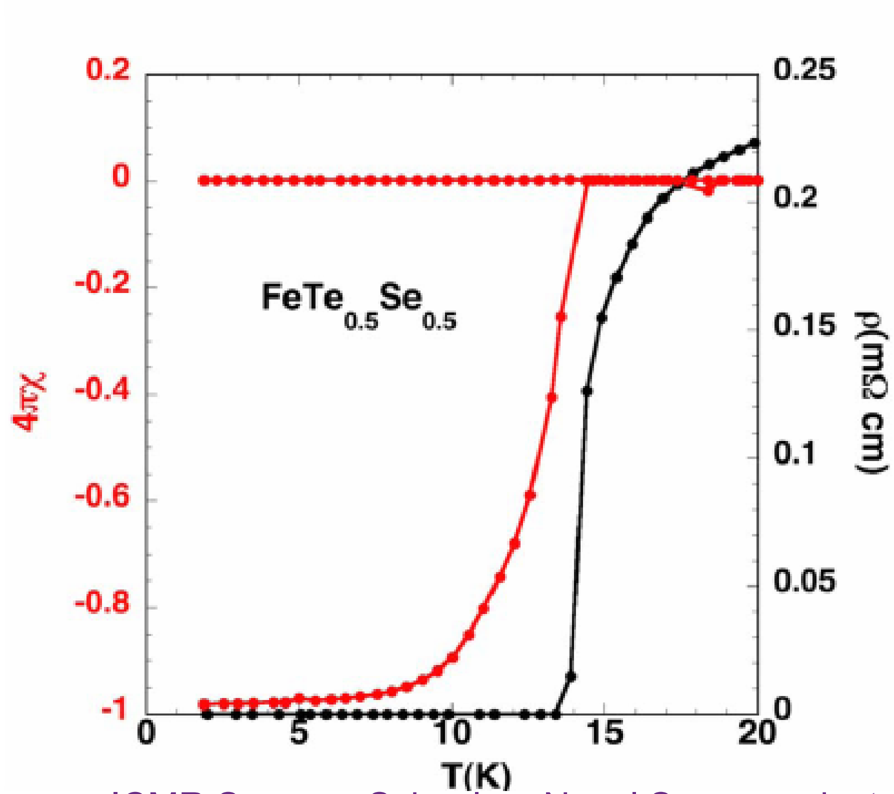
Bulk superconductivity at 14 K in single crystals of $Fe_{1+y}Te_xSe_{1-x}$

B. C. Sales, A. S. Sefat, M. A. McGuire, R. Y. Jin, and D. Mandrus
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Y. Mozharivskyj
Department of Chemistry, McMaster University, Hamilton, ON, Canada L8S 4M1

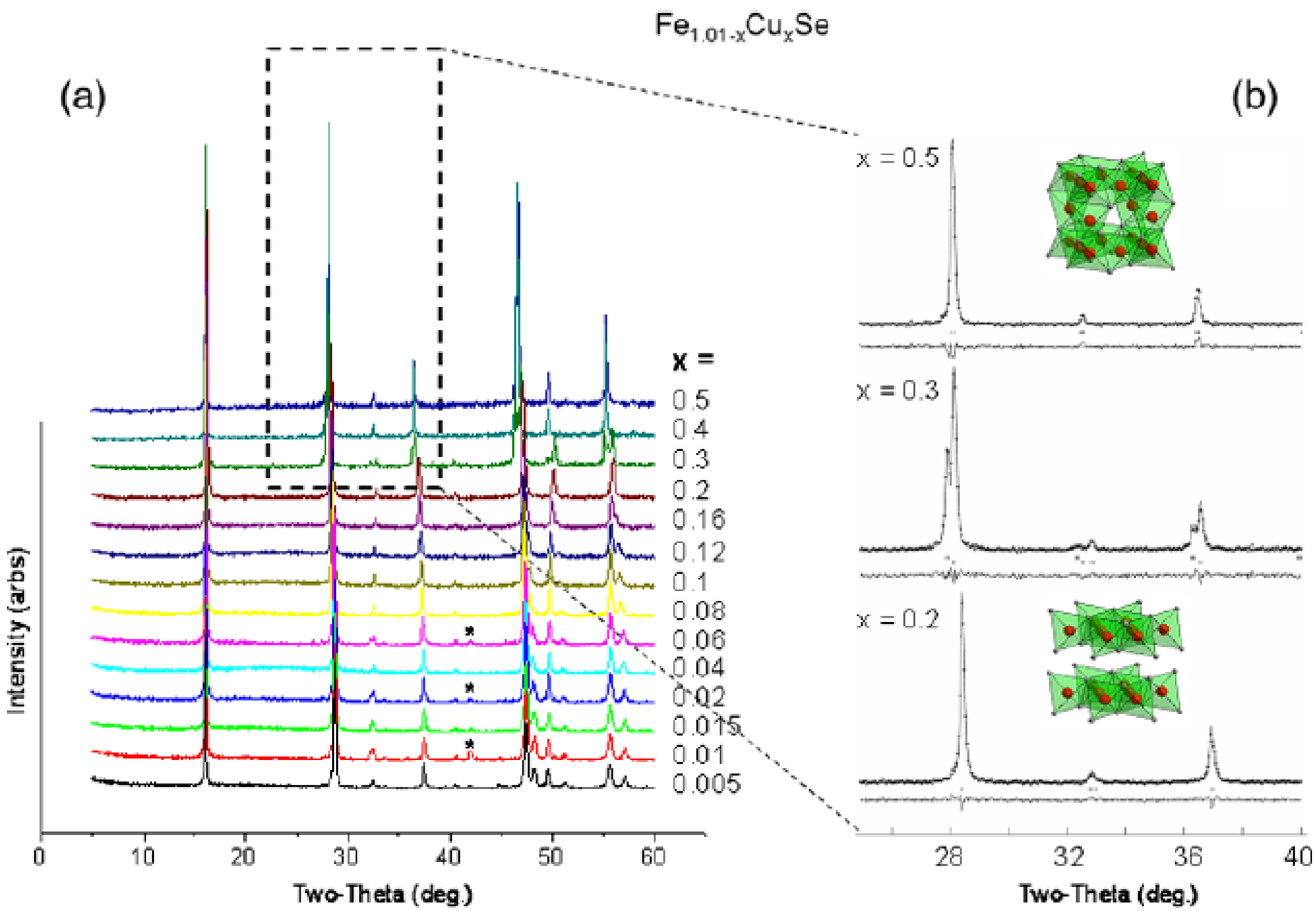
(Received 10 February 2009; published 24 March 2009)





Metal – Insulator Transition in $Fe_{1.01-x}Cu_xSe$

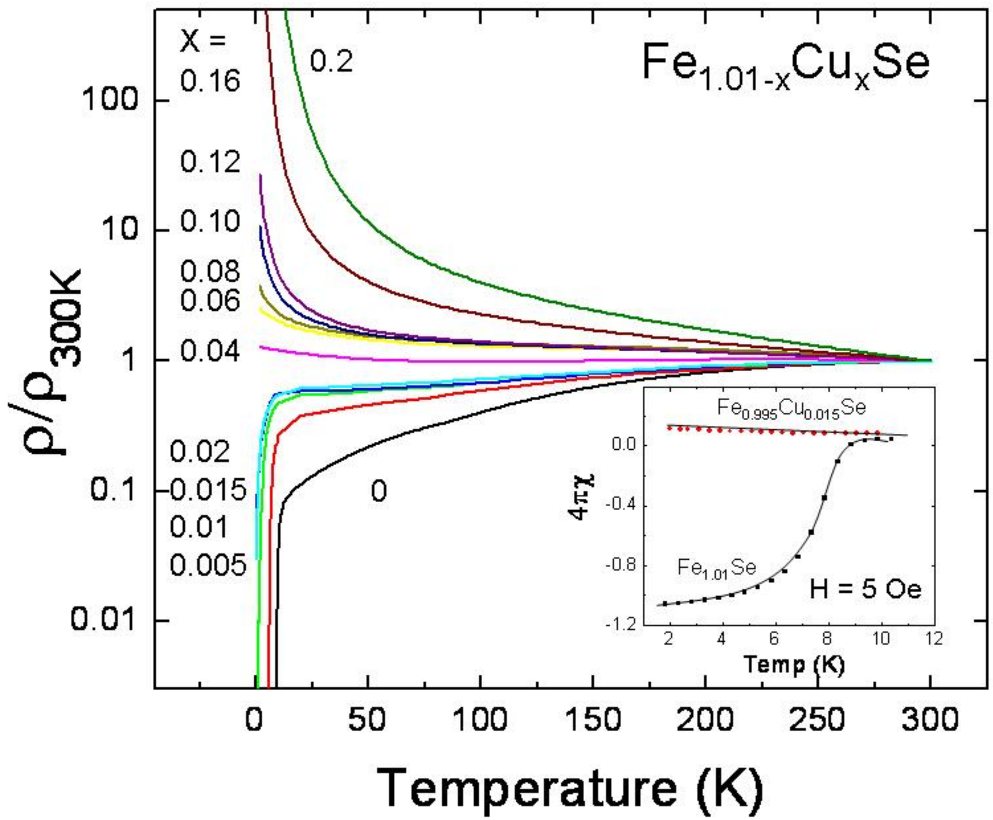
- Cu substitute Fe up to a solubility limit of 20–30%, after which a first-order transition to the three-dimensional $CuFeSe_2$ structure type is observed

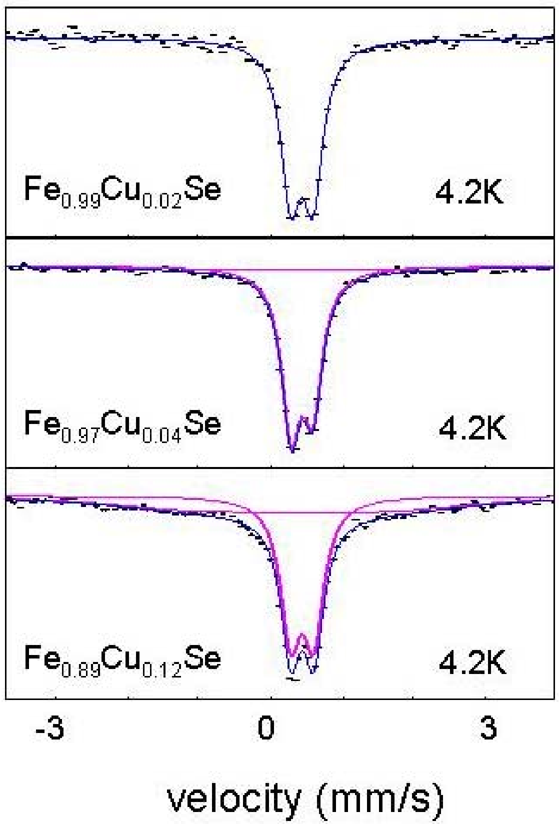


A J Williams et al. J. Phys.: Condens. Matter **21** (2009) 305701

Metal – Insulator Transition in $Fe_{1.01-x}Cu_xSe$

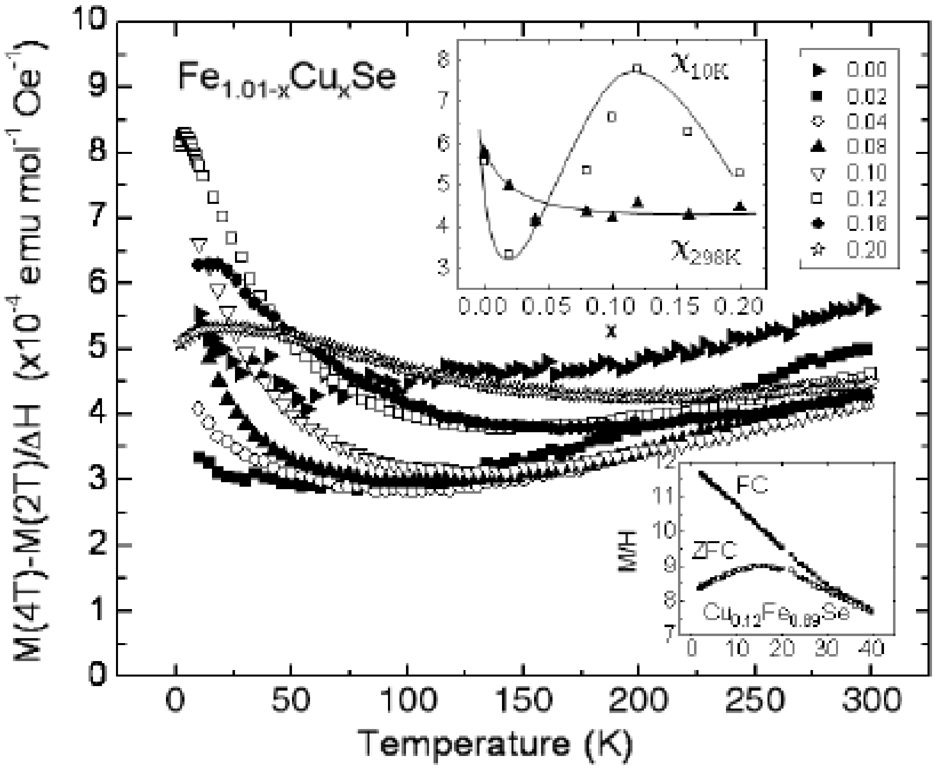
Cu doping changes the Fe-Fe distances
1% doping – no Meißner effect
Mott transition can be induced above 4% Cu doping





A J Williams et al. J. Phys.: Condens. Matter **21** (2009) 305701

Metal – Insulator Transition in $Fe_{1.01-x}Cu_xSe$



- Variation of magnetic susceptibility of the $Fe_{1.01-x}Cu_xSe$ samples with temperature
- A clear increase in the local moment with x is observed, culminating in a spin-glass-type transition at $Fe_{0.89}Cu_{0.12}Se$, which then broadens out at higher dopings.

This finding suggests that undoped FeSe superconductor is actually on the verge of an SDW ordering.

A J Williams et al. J. Phys.: Condens. Matter **21** (2009) 305701

IRON-BASED SUPERCONDUCTORS

Vital clues from a basic compound

Investigation of the phase diagram of the structurally simple compound FeSe may prove instrumental in raising the transition temperature in Fe-based superconductors and in understanding magnetic-mediated superconductivity.

Bernd Büchner and Christian Hess

Hence, not only is FeSe the prototypical new iron-based high-temperature superconductor, but it also seems to yield a simple and clear-cut example of "magnetism mediated superconductivity"[12],

What is different in FeSe compared to the ironpnictides

-highest TC among the binary SC

-FeSe is SC in the parent phase

-SC depends strongly on the stoichiometry

-The SC is connected to the tetra to ortho transition

-disappearance of SC is connected with the phase transition into NiAs

-no static magnetism over the whole phase diagram

-short range magnetic fluctuations

-pressure induced TC increase is not related to the suppression magnetism

–phonons and spin fluctuations play a crucial role for SC

Ingredients for high temperature superconductors (Mac Beasley)

-symmetry
-anisotropy
-short coherence length
(high N_EF, low v_EF)
-low charge carrier density

Does the structure type count?

Valence fluctuation – Superconductivity- Magneto resistance

Goal: rational Syntheses of Compounds with special electronic and magnetic properties

- Valence fluctuations
- Superconductivity
- Magneto resistance

- Same Structure type
- Electronic fingerprint

Valence fluctuation – Superconductivity- Magneto resistance

Perovskite		Cuprates Bismutates	Manganites
Inverse Perovskite	$EuPd_3B$	$MgNi_3C$	
Th_3P_4 $Pu_4(C_2)_3$	Eu_3S_4 $Rb_4(O_2)_3$	La_3S_4 $Y_4(C_2)_3$	Gd_3S_4
AlB_2	EuNiP	ZrRuP MgB_2	
TaS_2		$NbSe_2$	GdI_2
Heusler		Pd_2ZrAl	Co_2TiSn

Valence fluctuation – Superconductivity- Magneto resistance

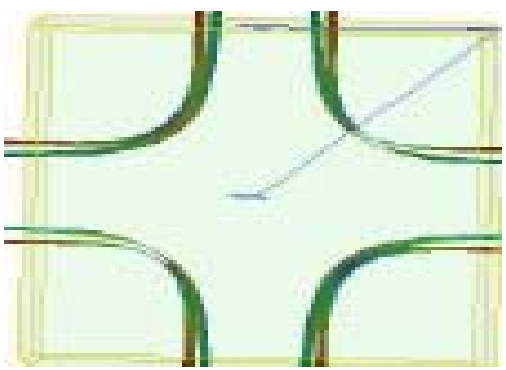
Spinell		$LiTi_2O_4$	Fe_3O_4
Cu_2Sb LiMnAs		NaAlSi LiFeAs	
$ThCr_2Si_2$	$EuNi_2P_2$ $EuCu_2Si_2$	$Ba_{1-x}KFe_2As_2$ $LuNi_2B_2C$ $LaRu_2P_2$	
…			

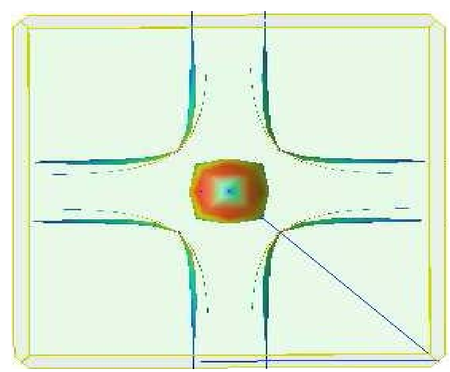
Theory and Experiment

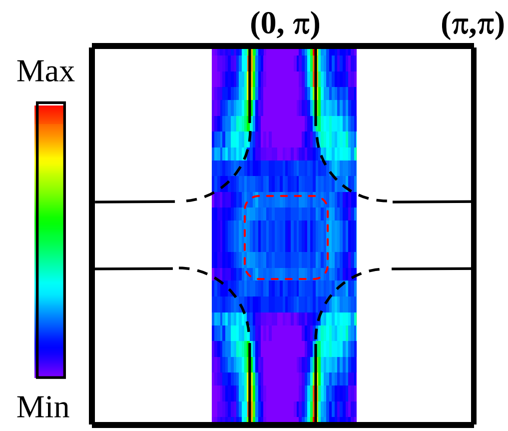
LDA-Fermi Surface

ARUPS

$La_{2-2x}Sr_{1+2x}Cu_2O_7$ $La_{2-2x}Sr_{1+2x}Mn_2O_7$







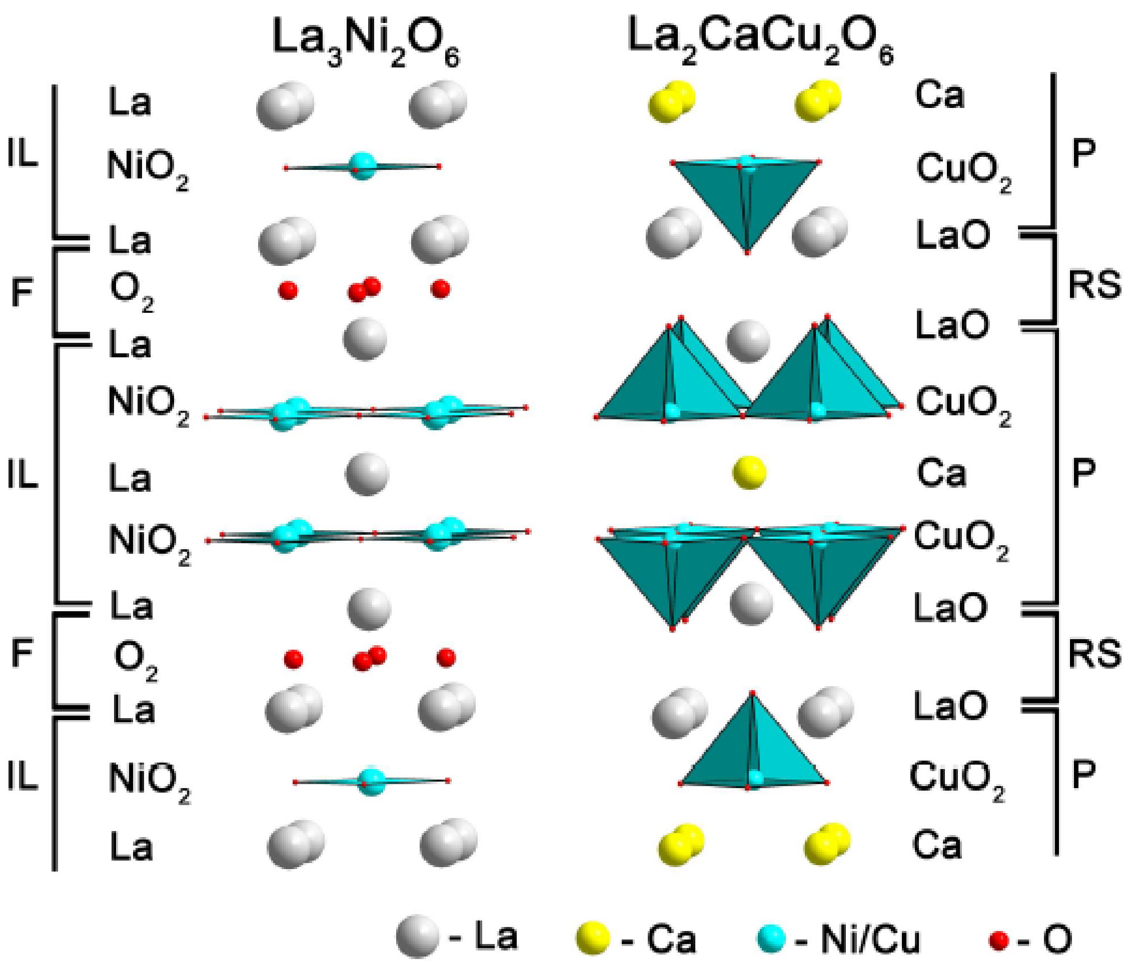
Dessau et al. priv. com. Colorado

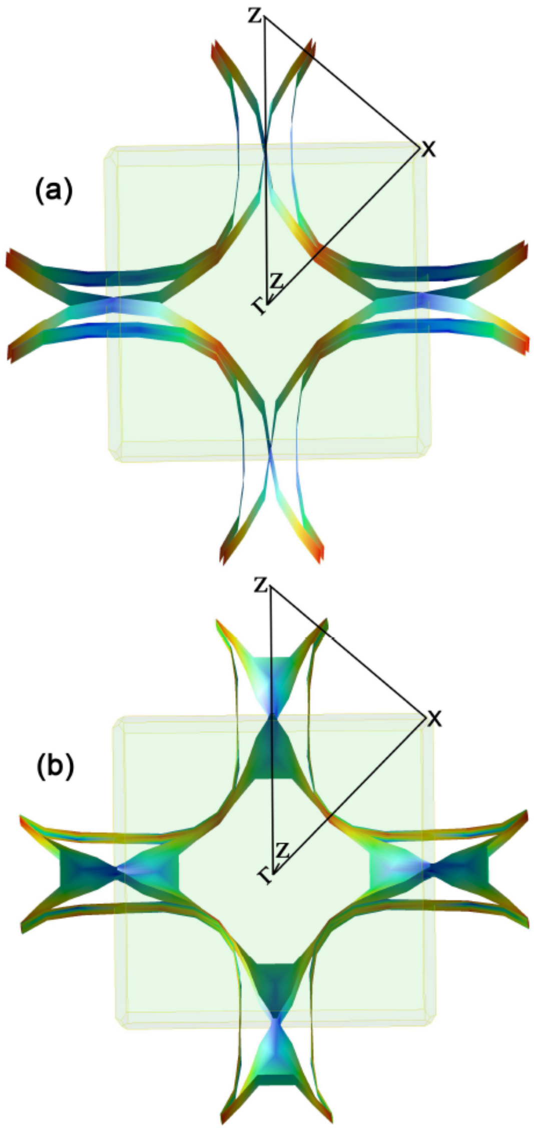
Mannella et al. NATURE 438 474(2005).

C. Felser et al., J. Mater. Chem 8 (1998)787

$Ni^{1,5+}$ - Nickelates: Candidates?

d^{9-d}: Ni^{2+} Ni^{+} vs. Cu^{3+} Cu^{2+}





V. V. Poltavets et al. Phys. Rev. Lett 102, 046405 (2009)

ELSEVIER

Journal of Alloys and Compounds 262–263 (1997) 87–91

Journal of ALLOYS AND COMPOUNDS

Valence instabilities and inhomogeneous mixed valence in some ternary eu...opium compounds

C. Fel...r

Ins... ...berg Universität Mainz, D-55099 Mainz, Germany

Superconductivity in La_3PdB and SrPdP

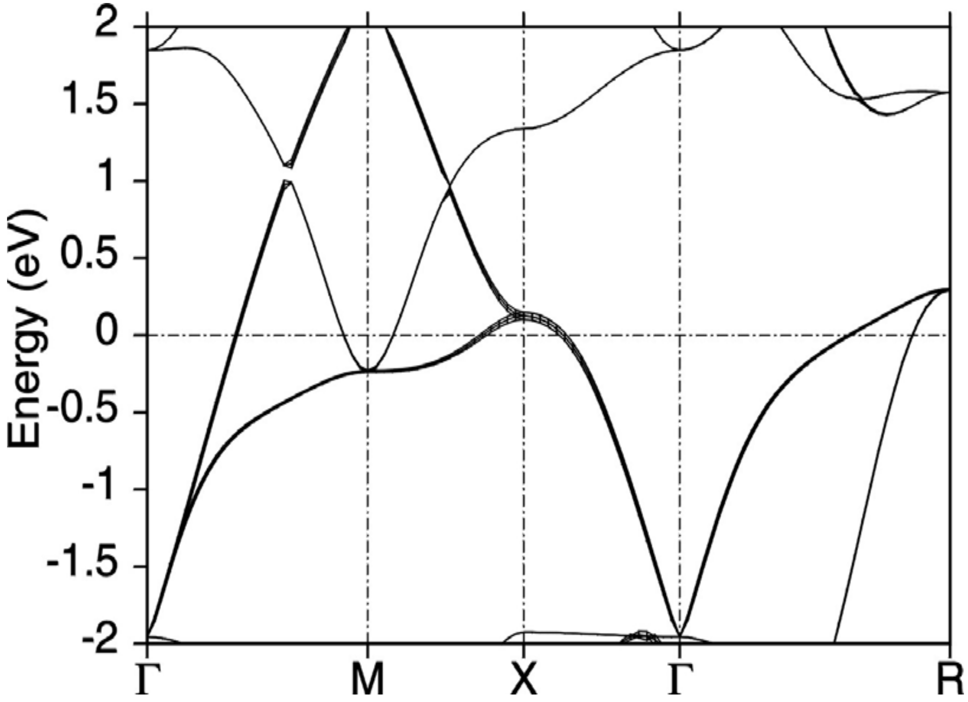
due to Eu 4f states. ... ...sumption that inhomogeneous mixed valency is an indicator for a vHS ... ...ds order anti-ferromagnetically at low temperatures, whereas La_3S_4 becom... ...cides with the Fermi level, whereas the singularity lies below the Fermi lev... ... van Hove scenario it must be possible to induce superconductivity via l... ...sevier Science S.A.

Valence fluctuations in Europium-compounds

moment

$EuPd_3B$: inhomogenous mixed valent

**C. Felser,
J. Alloys Compounds 61, (1997) 87.**

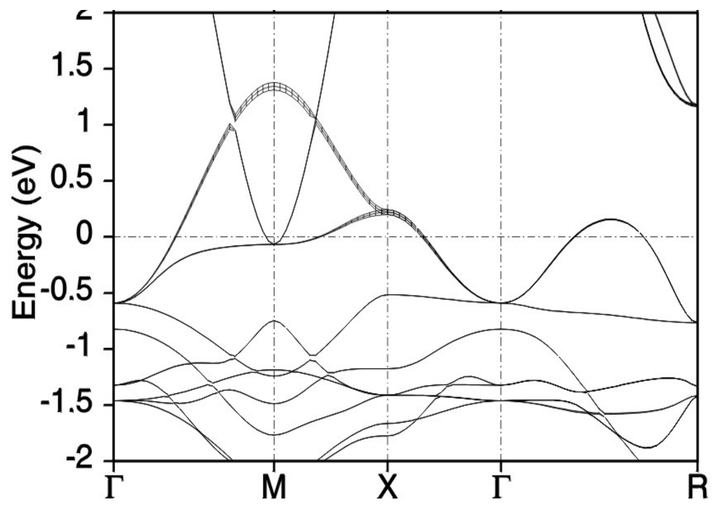


Prediction: Superconductivity in $LaPd_3B$

Superconductor

Superconductivity in the non-oxide perovskite $MgCNi_3$

T. He*, Q. Huang†, A. P. Ramirez‡, Y. Wang§, K. A. Regan*, N. Rogado*, M. A. Hayward*, M. K. Haas*, J. S. Slusky*, K. Inumara*, H. W. Zandbergen*, N. P. Ong§ & R. J. Cava*



$MgNi_3C$: isoelectronic to $LaPd_3B$
Three deimensional relative to $LuNi_2B_2C$

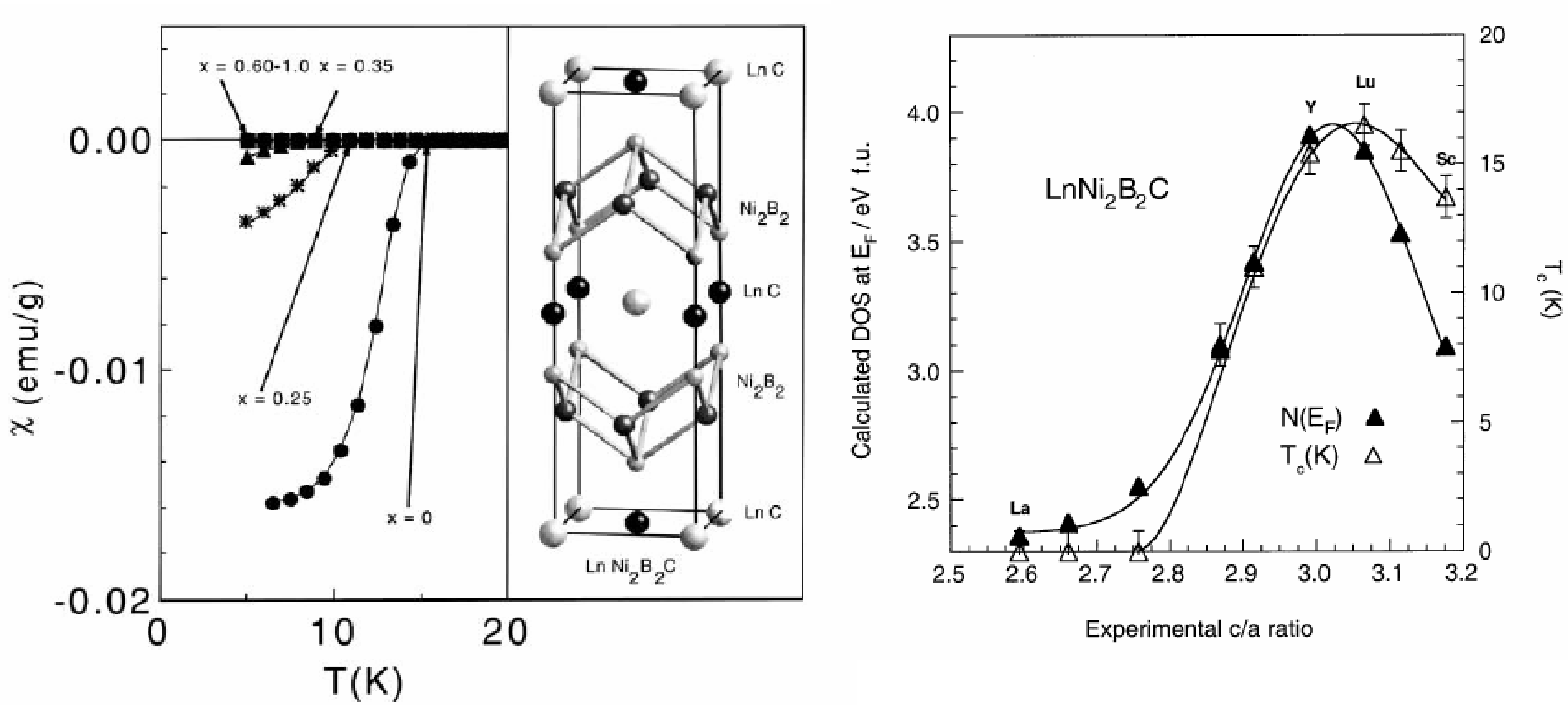
PERGAMON

Solid State Communications 119 (2001) 675–679

www.elsevier.com/locate/ssc

Structure and superconductivity in $LnNi_2B_2C$: comparison of calculation and experiment

S.M. Loureiro[a], C. Kealhofer[a], C. Felser[b], R.J. Cava[a,*]



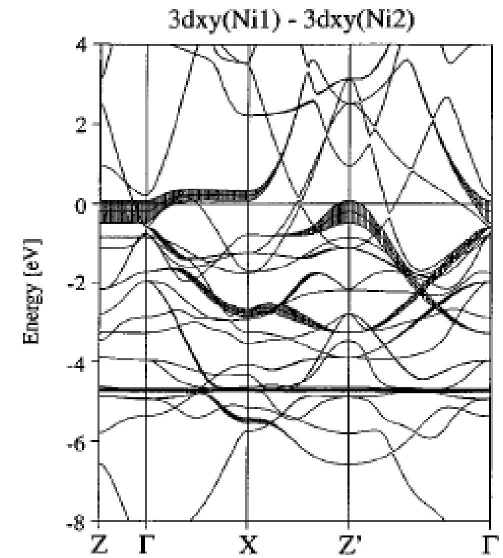
Relation between structure and T_C in the borocarbides

JOURNAL OF SOLID STATE CHEMISTRY **130**, 254–265 (1997)
ARTICLE NO. SC977300

LMTO Band Structure Calculations of $ThCr_2Si_2$-Type Transition Metal Compounds

Dirk Johrendt,*,†,[1] Claudia Felser,*,‡ Ove Jepsen,‡ Ole Krogh Andersen,‡ Albrecht Mewis,† and Jean Rouxel*

level by antibonding metal–nonmetal interactions. The band structures of superconducting $LuNi_2B_2C$ and nonsuperconducting $SrRh_2P_2$ are compared and their similarities are pointed out. A van Hove singularity, generated by metal–metal interaction, coincides with the Fermi level in $LuNi_2B_2C$ and lies about 0.2 eV higher in $SrRh_2P_2$. By doping, it should be possible to induce superconductivity in $SrRh_2P_2$ and related compounds. © 1997



May be the Ni – Ni distance counts